Support Information

Novel Fe$_3$O$_4$@GNF@SiO$_2$ nanocapsules fabricated through the combination of in-situ formation method and SiO$_2$ coating process for magnetic resonance imaging

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Experimental procedure

2.1 Materials

Iron(III) acetylacetonate (99.9%), Benzyl alcohol (99%), Benzyl ether (98%), Ammonium hydroxide solution (30-33% NH$_3$ in H$_2$O) and Tetraethyl orthosilicate (TEOS) (98%) were used as received from Sigma-Aldrich (Madrid Spain). Ethanol (absolute PA 99.5%) was used as received from PanReac AppliChem (Barcelona Spain). GNF were supplied by Pyrograf (USA), the type is PR-24-XT-LHT.

2.2 Steam cleaning process of GNF

GNF were initially purified following the standard steam cleaning process. As received GNF were placed into the center of a silica tube, which was then loaded into the alumina tube of a horizontal furnace. Steam was introduced by bubbling argon through hot water (98ºC). The whole system was initially purged by Ar for 2h to remove atmospheric air. Then the furnace was heated to 900ºC and held at this temperature for 1.5h. After the reaction, the furnace was cooled down to room temperature, and the resulting black solid was collected. Then, the GNF were dispersed in 100 mL of a 6 M hydrochloric acid solution and refluxed at 110ºC for 6h. Subsequently, the GNF sample was washed with water and filtered by using a polycarbonate membrane (0.2 μm pore size) until the pH=7. Finally, the sample were dried at 60ºC for 24 h.   We will refer to this sample as "steam treated GNF".

2.3 Acid treatment of GNF

In a typical process, 10 mg of steam cleaned GNF were dispersed in 10 mL HNO$_3$ with the aid of an ultrasonic bath for 2 h. The mixture was then transferred to a round bottom flask and refluxed at 140℃ for 16 h and then allowed to cool down to room temperature. The sample was washed with water and filtered by using Nylon membrane (200 ⬜m pore size) until the pH=7. After that, the black solid was collected from the top of the membrane and dried at 60ºC for 24 h. We will refer to this sample as "acid treated GNF".

2.4 Synthesis of Fe$_3$O$_4$@GNF nanocomposites

The acid treated GNF (1 mg) were dispersed in a solution (20 mL ethanol) containing the iron precursor (0.358 g Fe(acac)$_3$,1mmol) by ultrasonic treatment for 2 h, followed by magnetic stirring for 24 h. Afterwards, the mixture

was dried at 60ºC for 24 h (the solvent was totally evaporated), and the obtained solid was redispersed in 20mL of benzyl alcohol through ultrasonic treatment for 2 h, and stirred for 24 h. The solid was collected by centrifugation (10000 rpm, 30 min) and dispersed in 20 mL of benzyl ether. The Fe_3O_4 nanoparticles were prepared employing two different protocols. The first one involves traditional thermal annealing using a heating plate, where the iron precursor filled GNF are heated to 200ºC in benzyl ether in a round bottom flask at a heating rate of 1ºC/min and hold for 4 h under reflux. The second approach employs a microwave reactor with controlled atmosphere (Discover Explorer Hybrid from CEM Kamp-Lintfort Germany). The mixture is transferred into a microwave reaction vial where is rapidly heated to 200ºC and hold for 30min. In order to study the effect of the amount of $Fe(acac)_3$ on the final products, one mixture was prepared with only 0.0358g $Fe(acac)_3$ (0.1mmol) inside and the samples were synthesized via a traditional solvent thermal method.

In both synthesis, after the reaction the mixture was cooled to room temperature and washed. To do the washing process, 20 mL of ethanol were added to the mixture and an external magnet was applied to separate the solid, which was then redispersed in ethanol, and the process was repeated three times to get the Fe_3O_4@GNF. When necessary, the obtained samples were dispersed in ethanol for further characterization.

To shed some light on the role of the nitric acid treatment, an additional sample was prepared by applying the same experimental procedure, using a heating plate, on a sample of steam cleaned GNF.

2.5 Synthesis of Fe_3O_4@GNF@SiO_2 nanocapsules

The as synthesized Fe_3O_4@GNF hybrids were first dispersed in 10 mL of a ethanol/water mixture (v:v=10:1) containing 0.1 mL of ammonium hydroxide. Then 50 μL of TEOS (tetraethyl orthosilicate) was added into the solution which was kept stirring for 12 h. The products were isolated with the aid of an external magnet and washed several times with water and ethanol mixture (v_{water}:$v_{ethanol}$=1:1).

To confirm the sealing efficiency of the SiO_2 coating, a fraction of the sample was dispersed in an excess volume of HCl aqueous solution (pH = 2) and kept stirring for 2 h. The solid was collected by applying an external magnet and washed several times with water.

2.6 Characterization and Measurements

Fourier transform infrared spectroscopy (ATR-FT-IR) was performed on a Bruker Tensor 27 Fourier transform infrared spectrometer (Golden gate) in a range of 600-4000 cm^{-1}. All samples were measured as a solid powder at room temperature.

Transmission electron microscope (TEM) and high resolution transmission electron microscopy (HR-TEM) measurements were conducted on a JEOL 1210 TEM microscope operated at 130 kV and a JEM-2011 HR-TEM microscope at 200 kV. Electron energy loss spectroscopy (EELS) and Energy-dispersive X-ray spectroscopy (EDS) analysis (using High-angle annular dark-field imaging (HAADF)) were performed in a FEI Tecnai G2 F20 S-TWIN HR(S) TEM at 200 kV. For the analyses, one drop of the ethanol dispersion of the Fe_3O_4@GNF and the SiO_2 coated Fe_3O_4@GNF nanocomposites were independently deposited onto carbon-coated copper grids. In order to minimize the aggregation of the nanoparticles, the copper grids were laid on top of a filter paper during the drying process.

X-ray powder diffraction studies (XRD) were performed on D5000 Siemens X-Ray powder diffractometer in reflection mode using Cu Kα λ=1.5406 Å radiation in a range of $10° \leq 2\theta \leq 90°$.

Field-dependent magnetization curves were acquired by SQUID (Quantum design MPMS XL-7T) under a magnetic field from 0 to ±70000 Oe at 5K.

Thermogravimetric analyses (TGA) were carried out on a NETZSCH-STA 449 F1 Jupiter thermal analysis system from room temperature to 1000℃ under an O_2 flow.

Inductively coupled plasma mass spectrometry (ICP-MS) tests were carried out on an Agilent 7500ce analysis system.

Phantom MR imaging were performed at 7 T horizontal MR scanner (Bruker Biospec 7T MRI). The concentrations of Fe in the different samples were calculated according to the results from TGA and ICP-MS. Fe_3O_4@GNF and Fe_3O_4@GNF@SiO_2 nanocomposites were dispersed in a solution of 2% Pluronic F-127 for 30 min using a bath sonicator (Nahita Model I 610/3). Dispersed nanocomposites were mixed with an equal volume of melted agar solution (3%, w/v in water at 90℃) to achieve final Fe concentrations of Fe_3O_4@GNF nanocomposites and Fe_3O_4@GNF@SiO_2 nanocomposites ranging from 0.026 mM to 0.13 mM and 0.018mM to 0.09mM respectively in 1.5% agar in water.

References:

Cabana, L.; Ke, X.; Kepić, D.; Oro-Solé, J.; Tobías-Rossell, E.; Van Tendeloo, G.; Tobias, G., The role of steam treatment on the structure, purity and length distribution of multi-walled carbon nanotubes. Carbon 2015, 93, 1059-1067.
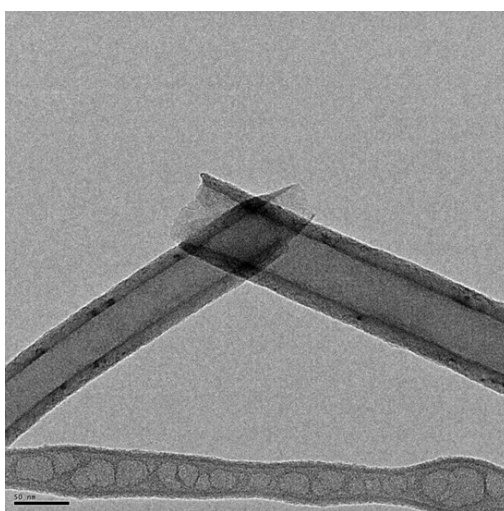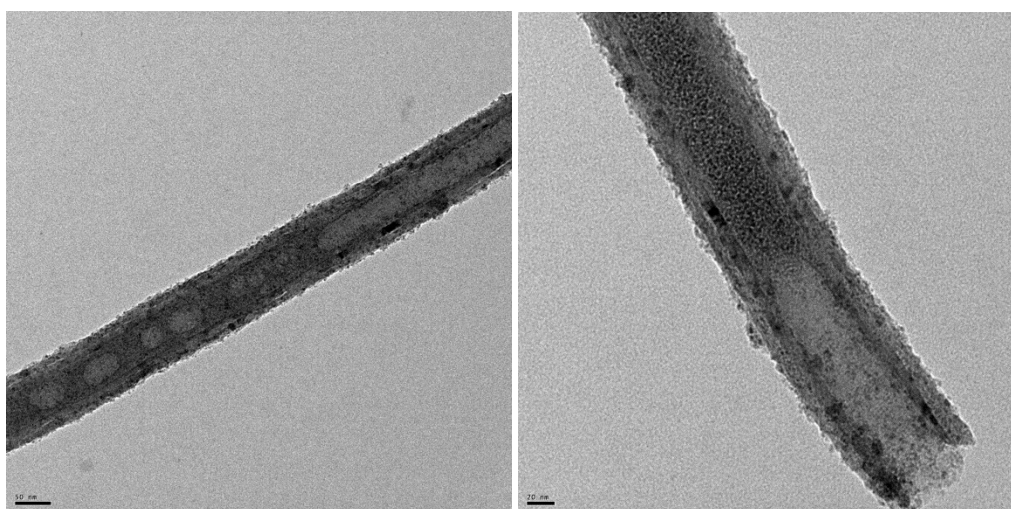
**Figure S1.** TEM image of the pristine CNF with open ends.
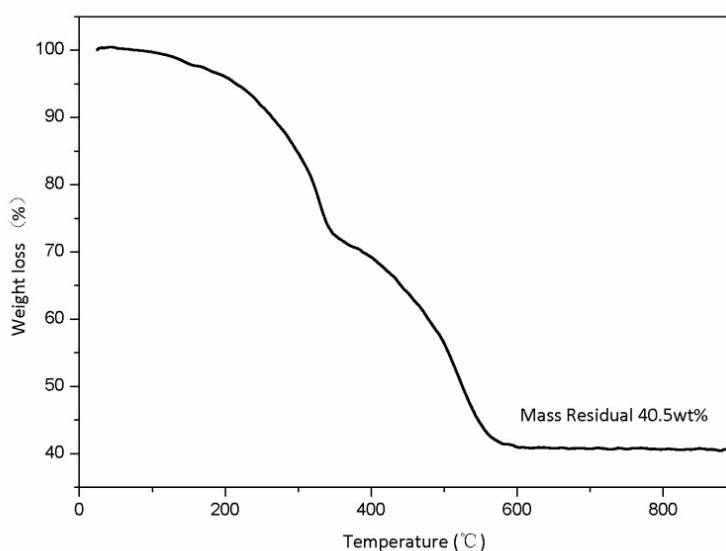
Figure S2. Thermogravimetric analysis under flowing oxygen of Fe_3O_4@GNF nanocomposites prepared using acid treated GNF by traditional thermal activation.
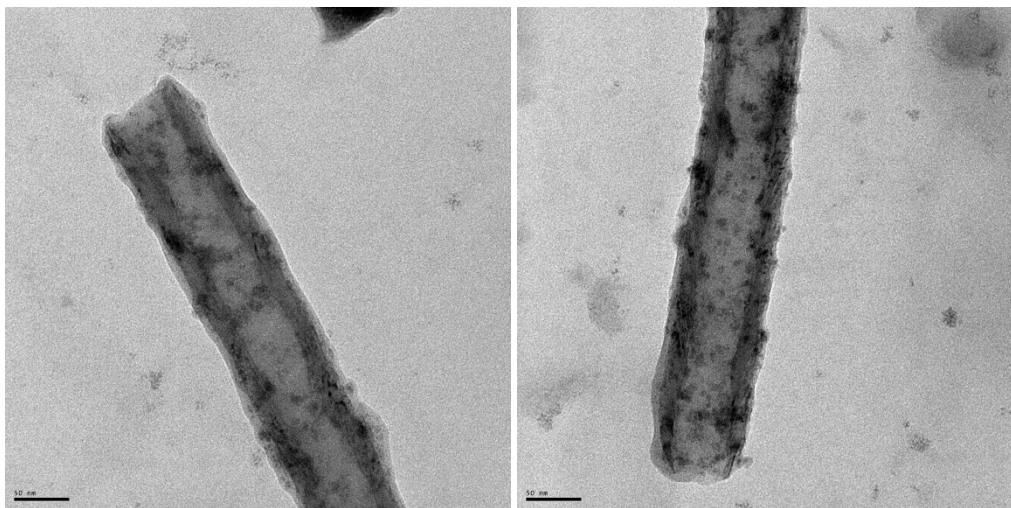
Figure S3. Fe$_3$O$_4$@GNF nanocomposites prepared using acid treated GNF, 0.0358g Fe(acac)$_3$ (0.1mmol) and standard thermal method.

Figure S4. Fe$_3$O$_4$@GNF nanocomposites prepared using acid treated GNF under microwave irradiation
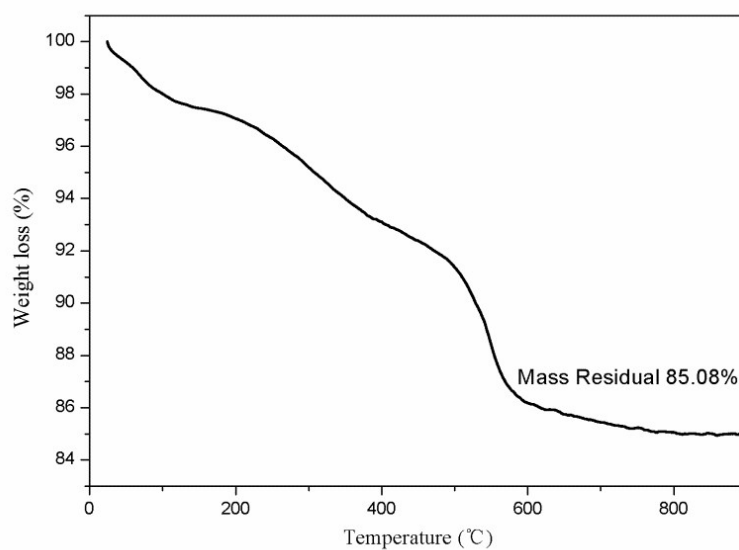
Figure S5. Thermogravimetric analysis of Fe$_3$O$_4$@GNF@SiO$_2$ nanocomposites under flowing oxygen.

Sample Name	Fe wt%	Si wt%
Fe_3O_4@GNF@SiO_2	4.9 %	19 %

Table S1. ICP-MS result of Fe_3O_4@GNF@SiO_2 nanocomposites