Influence of the graphitisation of hollow carbon nanofibers on their functionalisation and subsequent filling with metal nanoparticles.

Jean-Philippe Tessonnier[a], Dirk Rosenthal[a], Julien Amadou[b], Dominique Bégin[b], Cuong Pham-Huu[b], Dang Sheng Su[*a] and Robert Schlögl[a]

Electronic Supporting Information

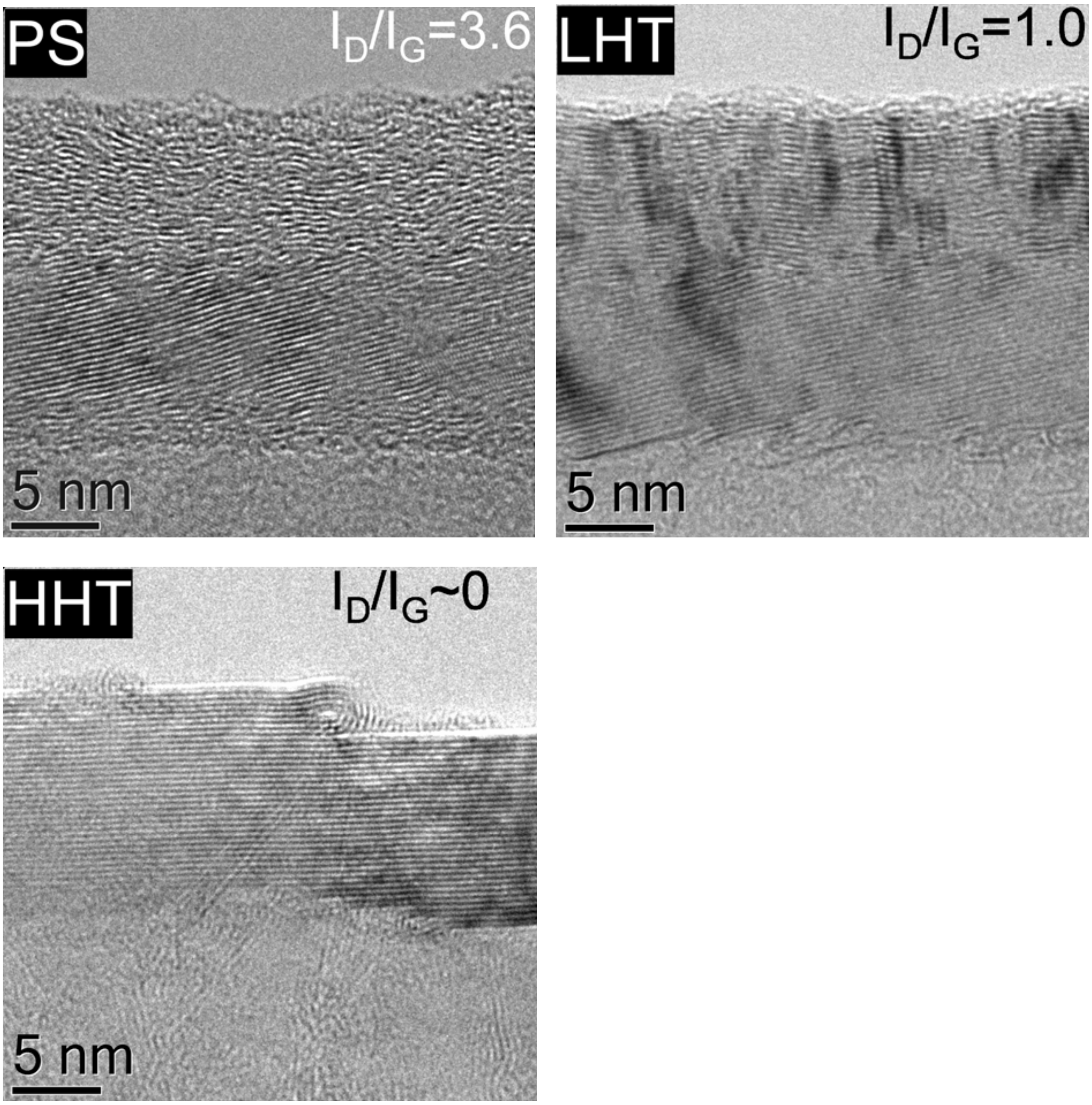

Figure 1. HRTEM images of the pristine supports.

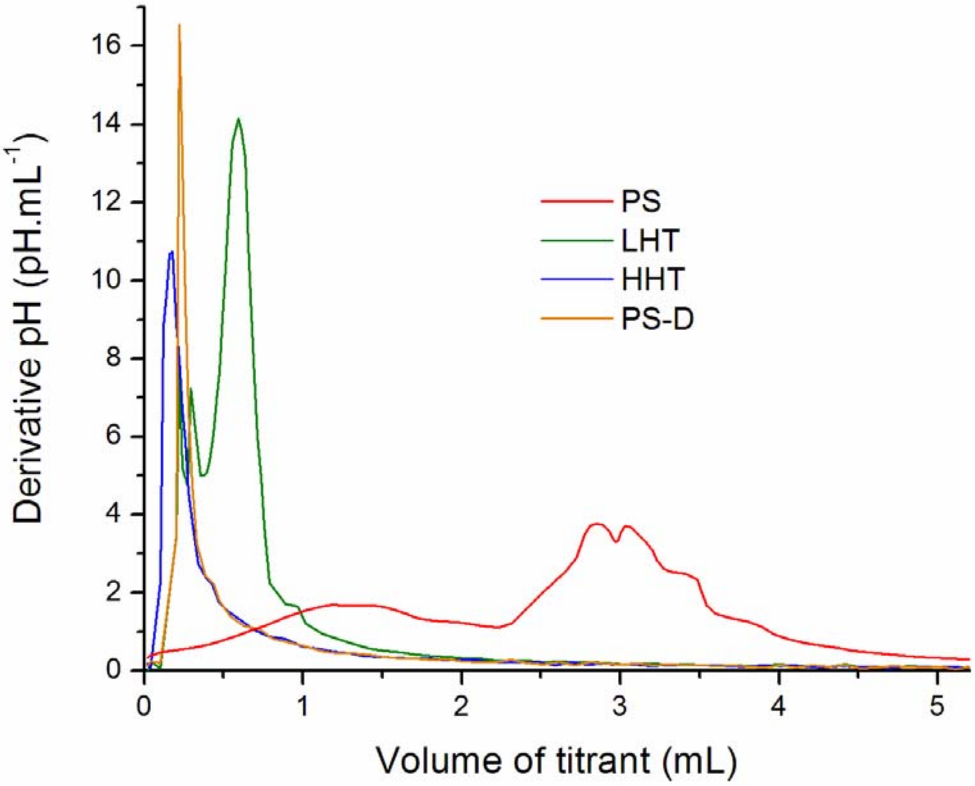

Figure 2. First derivatives of the acid-base titration curves obtained for the oxidised VGCNFs samples.

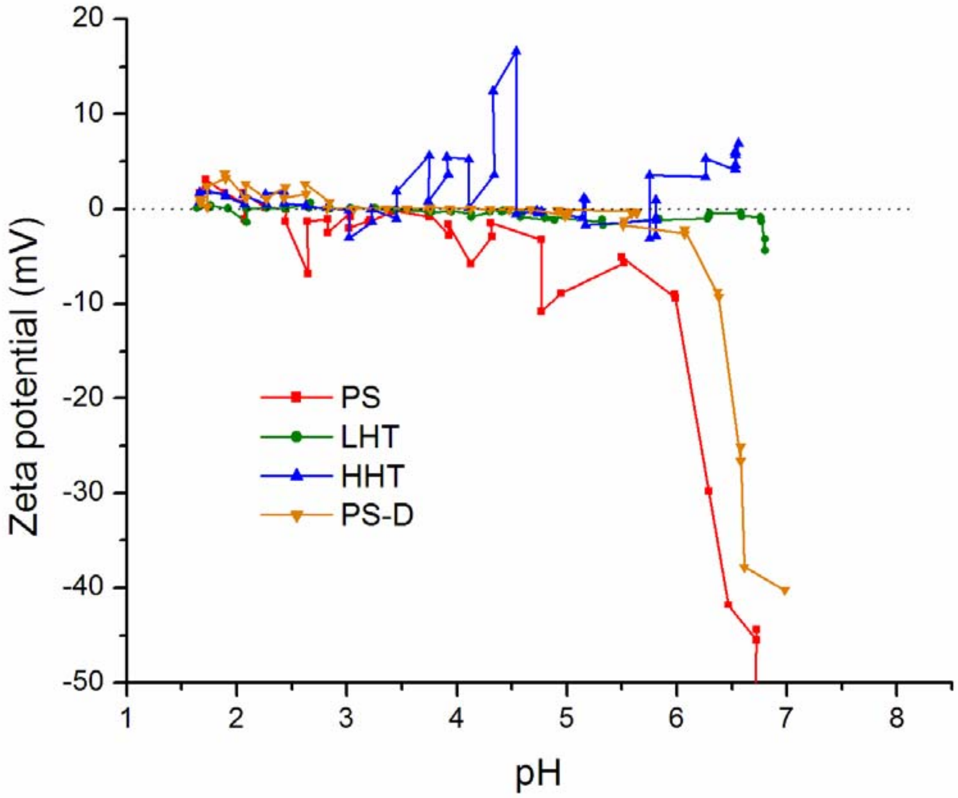

Figure 3. Zeta potential curves measured for the different oxidised VGCNFs samples. The scattering for the HHT sample is due to the low number of surface functional groups.

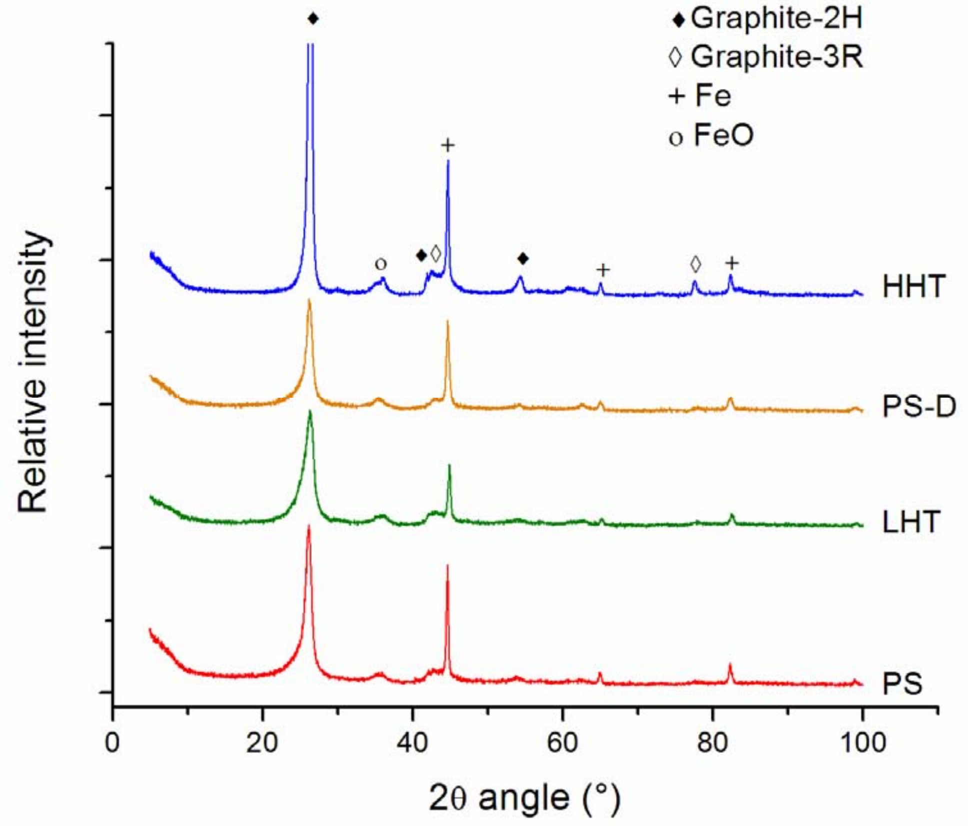

Figure 4. XRD patterns of the Fe/VGCNFs samples. The presence of FeO peaks is due to the oxidation of the surface of the iron particles upon exposure to air.

Experimental details

Vapor-grown carbon nanofibers (VGCNFs) were purchased from Pyrograf Products Inc. (Ohio, USA. Products PR24-PS, PR24-LHT and PR24-HHT). Details about their synthesis and structure can be found elsewhere[13]. Shortly, the VGCNFs were synthesised by chemical vapour deposition (CVD) using methane as a carbon source. The as-grown VGCNFs were subsequently post-treated in inert atmosphere at 700 °C (PS), 1500 °C (LHT) or 3000 °C (HHT) to increase their graphitic character. The purchased VGCNFs products were treated with concentrated nitric acid (70%, Sigma-Aldrich) under vigorous magnetic stirring at 100 °C for 10 h. The treatment was performed at a temperature below the boiling point of nitric acid (130 °C) to avoid thermal degradation of HNO_3 and loss as gaseous NO_2. The ratio of nitric acid to carbon sample was set to 500 mL for 10 g. This ratio was expected to be sufficient to avoid changes in the nitric acid concentration due to consumption. After treatment, the solution was allowed to cool down to room temperature. It was then filtered and the carbon sample was thoroughly rinsed with 1 L distilled water.
Iron nanoparticles were deposited on the VGCNFs using the incipient wetness impregnation technique. Briefly, 803 mg of $Fe(NO_3)_3 \cdot 9\ H_2O$ (Sigma-Aldrich) were dissolved in 6 mL distilled water and added drop wise to 1 g of VGCNFs. The samples were then dried at 50 °C for 10 h, calcined in static air at 350 °C for 2 h (heating ramp: 10 °C/min) in order to decompose the iron precursor and form iron oxide particles. Finally, the samples were reduced in flowing hydrogen (50 mL/min) at 400 °C for 2 h (heating ramp: 10 °C/min).

The transmission electron microscopy (TEM) investigation was conducted in a Philips CM200 TEM with a LaB_6 emitter. The samples were dispersed in chloroform and deposited on a holey carbon film supported on a Cu grid.

Thermogravimetric analysis (TGA) of the samples was carried out with a Netzsch STA 449 thermobalance for simultaneous TG-DSC. The TGA experiments were carried out using a 100 $mL.min^{-1}$ flow of Ar. The temperature was ramped from 30 to 1150 °C at 2 $°C.min^{-1}$.

XP spectra were recorded at room temperature, using non-monochromatized Mg Kα radiation (1253.6 eV) for excitation and a hemispherical analyzer (Phoibos 150, SPECS). The binding energy scale was calibrated with $Au4f_{7/2}$ (84.0 eV) and $Cu2p_{3/2}$ (932.7 eV) The O1s spectra were compared after subtraction of a Shirley background. The ratio of oxygen to carbon was obtained by assuming a homogenous distribution model.[13]

Titrations were performed with a Mettler DL 77 automatic titrator equipped with a Mettler-Toledo DGi114-SC electrode and controlled with the LabX software of the same company. Typically, 100 mg of sample were dispersed in 50 mL of a 10^{-3} M KCl solution. The mixture was kept under vigorous stirring overnight. Prior to measurement, the mixture was degassed under Ar for at least 1 h, until the pH value was constant. The titration was then performed under Ar, using a 10^{-2} M NaOH solution.

Zeta potential measurements were performed using a Malvern Instruments Ltd. ZEN 3600 Zetasizer, equipped with a 633 nm laser, in combination with a MPT-2 auto-titrator. A small amount of sample was first dispersed in distilled water with the help of an ultrasonic bath. The solution was then filtered with a 5 µm filter in order to remove aggregates. The measurements were performed with a DTS 1060C cell at a constant temperature of 25 °C. The pH of the solution was decreased from pH 7 to pH 1.5 with a step of 0.2 using a 0.01 M HCl solution. A delay of 20 s was allowed between each measurement. Data were acquired and analyzed with the Marvin software from the same company.

X-ray diffraction powder patterns (XRD) were measured with a Bruker D8 Advanced diffractometer, using Cu Kα radiation. Processing of XRD data was performed using the

Bruker powder diffraction software package TOPAS. The phases were identified by comparison with the data reported in the ICDD database.