Electronic Supplementary Material (ESI) for ChemComm.

Experimental:

Mixtures of dichlorobenzene (0.65 mL) and ferrocene (1 gram) were evaporated and pyrolyzed in a CVD system comprising a quartz-tube reactor of 1.5 m (inner diameter of approximately 40 mm), smooth Si/SiO_2 substrates (4 cm length, 2.5 cm width and 0.525 mm thickness) and an electrical furnace with a temperature of 990 ^{o}C. The evaporation temperatures used in the reactions were 120 ^{o}C and 90 ^{o}C. Two types of Ar flow rates (laminar flow) were used: 20 mL/min and 100 mL/min. The reaction time was 1 hour. The sample was cooled down by removing the furnace along a rail system (quench). The buckypapers were then peeled off from the Si/SiO_2 substrates and washed in distillate water. SEM and backscattered electrons investigations were performed with a JSM-7500F at 10-20 kV. TEM was performed with a 300 kV American FEI Tecnai F30. XRD analyses were performed with an Empyrean Panalytical diffractometer (Cu K-α with λ = 0.154 nm). XPS measurements were performed with an Axis Ultra KRATOS with a maximum penetration depth of 10 nm. The pore size distribution was measured with a Quadrasorb SI automated Surface Area and Pore Size analyser. The Raman measurements were performed with a Horiba Jobin Yvon HR Evolution. The magnetic measurements were performed at room temperature with a VSM at 1.3 Tesla. The metal content of the CNTs was measured with a Mettler Toledo TGA/DSC 2/1600 Thermastar. Seebeck coefficient measurements were performed with a MMR SB100 measurement system.

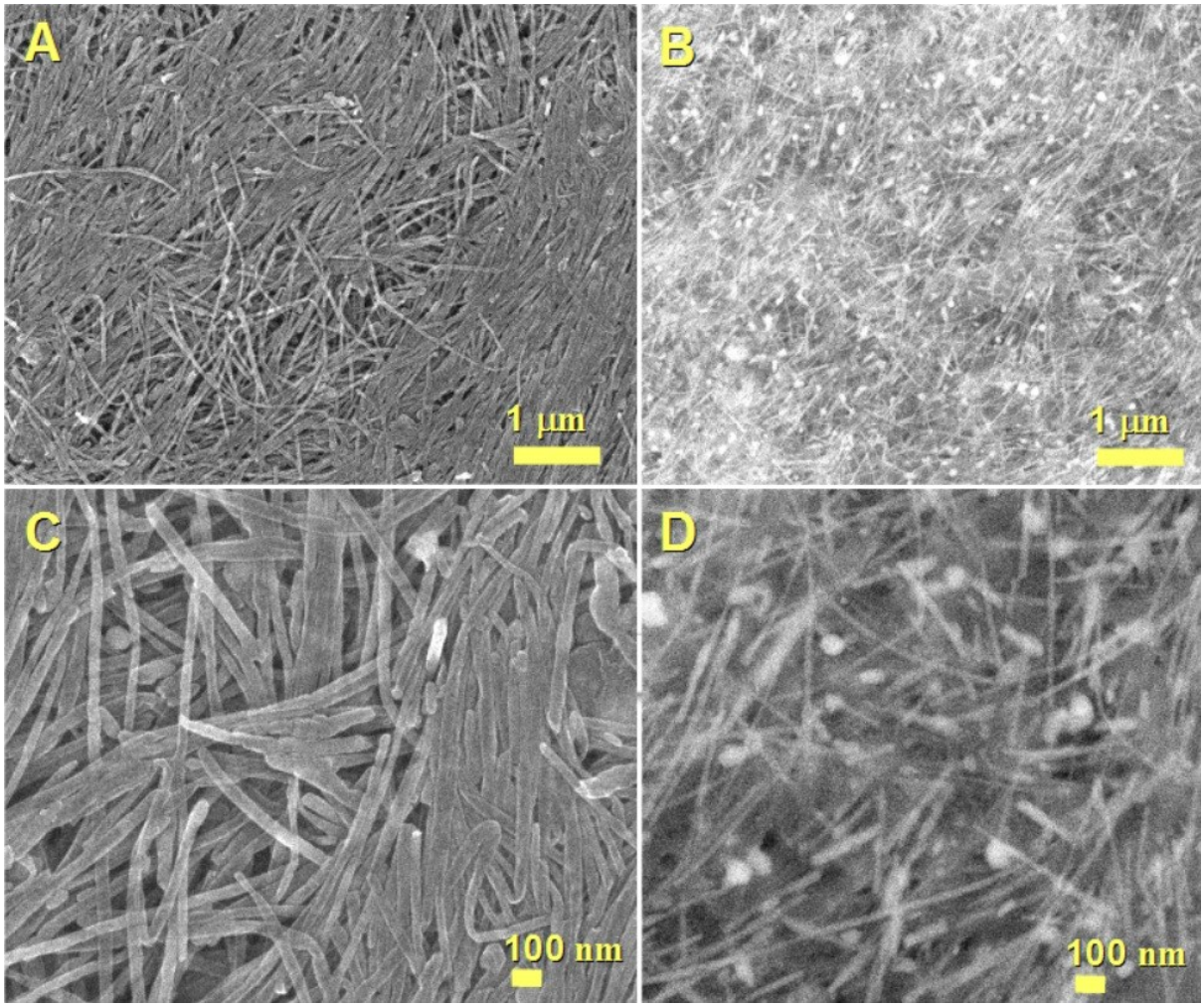

Figure 1 Supp: SEM micrographs (A-C) showing the random orientation of the CNTs comprised in the buckypaper obtained with vapour flow rate of 20 mL/min and evaporation temperature of 120 ^{o}C. In D the very high filling rate of the CNTs is shown with high detail through BE analyses.

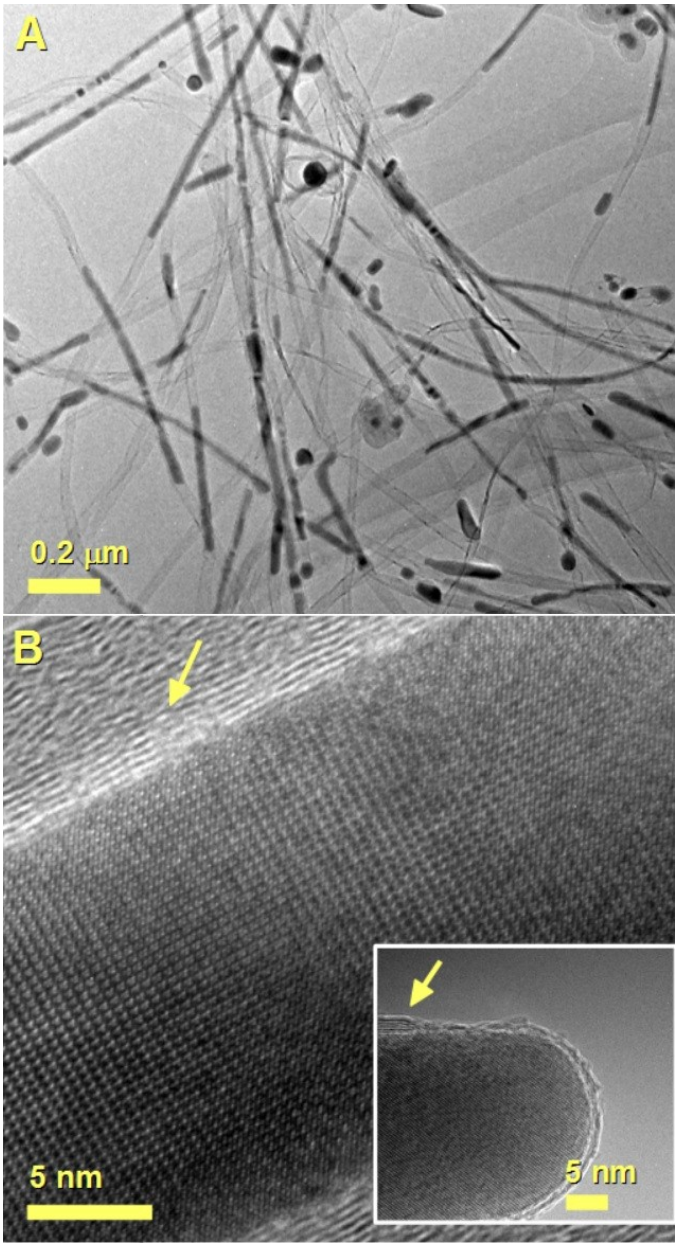

Figure 2 Supp: TEM micrographs (A) and HRTEM micrographs (B-C) showing the Fe_3C- filling rates of the CNTs obtained with a flow rate of 20 mL/min and evaporation temperature of 120 ^{o}C. Note that the yellow arrows show the variation of the CNTs walls number along the tube and in the CNTs-cap (see inset). The lower number of CNTs walls observed in the CNT cap can be associated to the etching interaction with Cl radicals in the CVD-reactor during the growth. In B the lattice spacings of 0.4 nm and 0.5 nm corresponding to the 001 and 100 reflections of Fe_3C were measured.

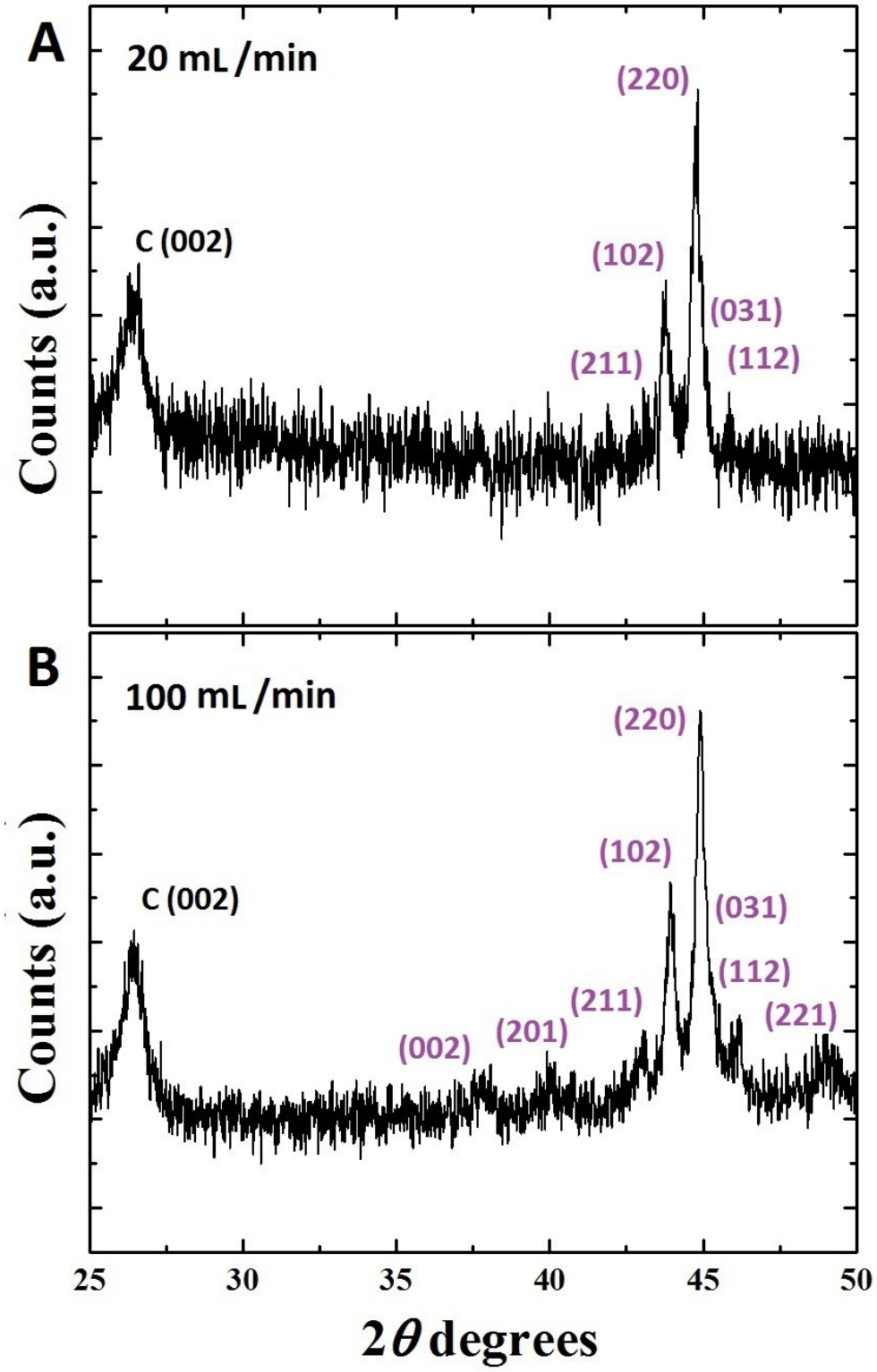

Figure 3 Supp: XRD analyses of the buckypapers produced with vapour flow rates of 20 mL/min (A) and 100 mL/min (B) showing the presence of preferred plane-orientations of the crystals inside the CNT capillary. The graphitic structure of the CNTs is identified by the 002 plane reflection.

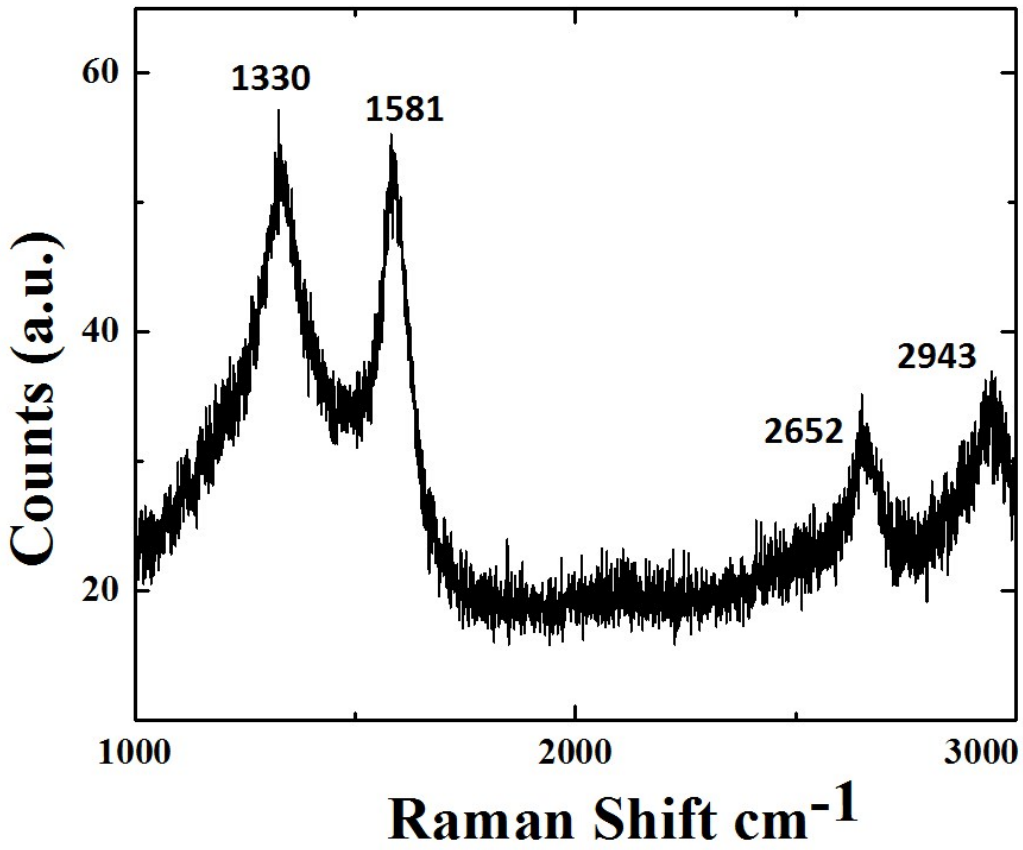

Figure 4 Supp: Raman Spectrum of a typical horizontally aligned filled CNTs buckypaper. The peak observed at 1330 cm^{-1} refers to the D band and is associated to the disordered induced scattering produced by imperfections or loss of hexagonal symmetry in the carbon structure, the peak observed at 1581 cm^{-1} refers to the G band and is associated to the Raman active $2E_{2g}$ mode which is generally observed in graphite like materials. The peak observed at 2652 cm^{-1} refers to the 2D band while the peak at 2943 cm^{-1} refers to the combination of the D+G band.

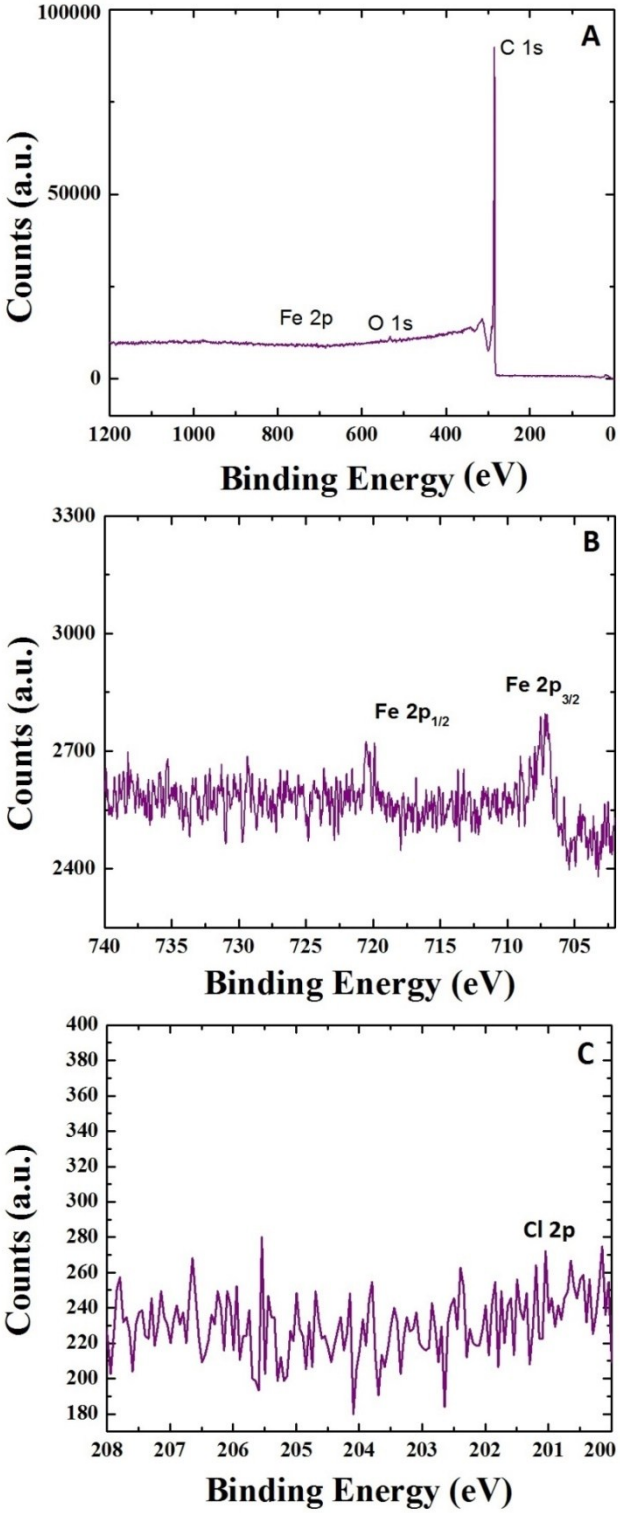

Figure 5 Supp: XPS spectra of a typical buckypaper consisting of horizontally aligned filled CNTs. The Spectra show in A the presence of carbon due to the contribution of the CNTs walls. Note that the penetration depth of the X-rays in this technique is below 10 nm (much lower than that of X-rays in the XRD measurements which is in the order of many micrometres, 8-10 micrometres). Considering that the thickness of the CNTs walls is in the order of 5-8 nm the signal of the Fe_3C crystal encapsulated inside the CNTs is expected to be low. The high detail of the XPS measurement in the range of 740-700 eV in B confirms this interpretation with low Fe $2p_{1/2}$ and Fe $2p_{3/2}$ peaks. In C the XPS spectra in the range of 208-200 eV shows that no Cl residues are found in the

buckypaper surface. The small oxygen peak observed in A can be associated to the oxygen adsorbed by the porous structure of the buckypaper when exposed in air.

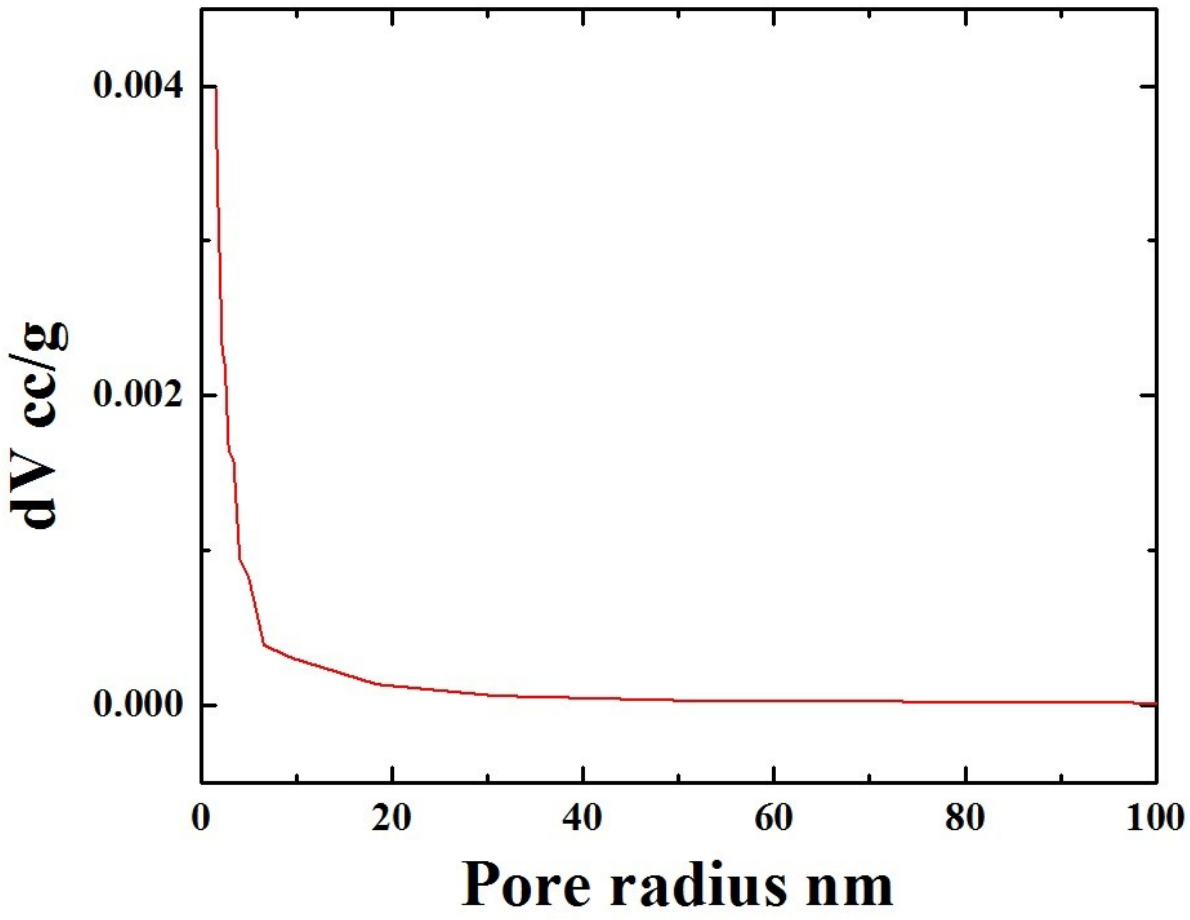

Figure 6 Supp: Porosity measurement of a typical buckypaper comprising horizontally aligned Fe_3C filled CNTs showing the presence of a pore-radius below 1.5 nm. Note that due to the instrumental limitation, porosity values below 1.5 nm could not be well resolved.