SUPPORTING INFORMATION

Single Step, High Yield, Controlled Synthesis of Graphitic Networks from Dense Microemulsions

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Experimental

Materials: Chemicals were purchased from Sigma-Aldrich BV and used as received: the surfactants, sodium bis(2-ethylhexyl)sulphosuccinate (Na-AOT, 99%) and 4-(1,1,3,3-Tetramethylbutyl)phenyl-polyethylene glycol (Triton-X 100, 99.999%); the solvents, n-heptane (99.9%) and toluene (\geq 99.5%); the metal precursors, chloroplatinic acid hydrate (99.9%), iron chloride (\geq 99%), cobalt acetate tetrahydrate (99.999%), nickel chloride (99.99%); the reducing agents, hydrazine hydrate (solution in water, 35% in weight), sodium borohydride (granular, \geq 98%); nitric acid (70%) and sulphuric acid (95-98%). Water produced by Milli-Q Ultra-Pure-Water system of Millipore BV was used in all sample formulations. The support used were: titanium grids and silicon wafers, ST Instruments BV; carbon black, Vulcan® XC72R, Cabot Corporation; carbon paper, Alfa Aesar; ceramic crucibles (10cm x 2cm), Fisher Emergo BV.

Catalyst Preparation and Support Transfer: The method followed here is based on previous work.¹ Briefly, BMEs were prepared by mixing water/Na-AOT/n-heptane or water/Triton-X/toluene in the ratio 0.2/0.53/0.27 or 0.2/0.64/0.16 respectively in weight. For each synthesis, two BMEs were prepared, one containing the metal precursor and one, containing 10 times excess of reducing agent dissolved in the water phase. Concentrations are always specified with respect to the amount of water in the BMEs. After an arbitrary waiting time of one hour, they were mixed and left overnight to complete the reaction. The BME containing the catalyst was directly loaded on silicium, titanium or carbon paper support. When the synthesis was carried out in bulk, BMEs were directly loaded on ceramic crucibles.

Chemical Vapor Deposition: CVD was carried out in a quartz tube reactor of inner diameter 80 mm mounted in a 5-zone tube furnace from P-KEM Ltd. BME containing catalyst was placed over the support in the hot-zone of the reactor. For the production, the temperature was raised to 700 °C (10 °C min⁻¹) under nitrogen (N₂) flow at 160 ml min⁻¹, phase 1 in Fig. 2b. Ethene gas (C_2H_4) was introduced at 96 ml min⁻¹ (60 or 120 when the ethene flux influence was investigated) for 60 min at 700 °C, phase 2 in Fig. 2b. Finally, the ethene gas flow was stopped and the reactor was cooled down to room temperature under nitrogen flow. When annealing treatment was performed, after stopping ethene gas the reactor was purged with N_2 for 30 min, phase 3 in Fig. 2b, then temperature was raised to 1000°C (10°C min⁻¹), phase 4 in Fig. 2b, and maintained for 60 min, phase 5 in Fig. 2b. Afterwards the reactor was cooled down to room temperature under N_2 flow for approximately 150 min, phase 6 in Fig. 2b. All gases were introduced at atmospheric pressure. CNNs synthetized over silicon wafer and TEM grids were analysed as recovered from the reactor without washing. CNNs synthetized on carbon paper were washed three times with acetone and water and then used for further analysis. Bulk CNNs samples were collected as an agglomerated powder. The samples were purified of tar, polyaromatic hydrocarbons (PAHs), and

inorganic impurities firstly by washing several times with acetone, and secondly by an acid washing (HNO_3) combined with sonication for 30 min.

Instrumentation: A scanning electron microscope (SEM, JEOL JSM-6010LA) and a Transmission Electron Microscope (TEM, Philips CM30T) equipped with an energy dispersive spectrometer (EDS) were used to investigate the structural morphologies of the samples and perform elemental analyses. Raman scattering spectroscopy (System 2000, Renishaw Public Limited Company) with a laser excitation wavelength of 514 nm was used to investigate carbon hybridization and defects amount. Thermogravimetric Analysis (TGA, Mettler-Toledo TGA/SDTA 851) was performed to quantify temperature resistance under inert (N_2) and oxidizing (air) atmosphere. Specific surface area was obtained from the N₂ isotherm, obtained at 77 K with an Autosorb-1C setup from Quantachrome Instruments, using the Brunauer Emmett Teller (BET) method. Electrochemical surface area was measured performing cyclic voltammetry in 0.5 M H₂SO₄, N₂ saturated, scan rate 20 mV s⁻¹, with a µAutolab Metrohm potentiostat. Experiments were conducted in a conventional three-electrode cell, using a Reversible Hydrogen Electrode (RHE) as reference and a Pt wire as counter electrode. The working electrode was the carbon paper or CNNs grown on carbon paper, loaded in a Teflon mask of area 1 cm² and in contact with a copper wire on the back. On dielectric spectroscopy (Novocontrol) frequency was measured between 1 mHz and 1 MHz. CNNs were loaded in a sample holder of 13 mm in diameter with 2.04 mm thickness. No pressure was applied.



Figure S1. TEM Images of branches (1,2) junctions (3,4,5).



Figure S2. SEM Images of junctions of CNNs synthetized with annealing (a-h) and without annealing (i-m).



Figure S3. TGA profiles for BME decomposition in nitrogen (a) for systems composed of water/Na-AOT/n-heptane (red) and of water/Triton-X100/toluene (black), where metal NPs (Pt catalyst) have been synthetized starting from 50 mM and 30 mM of Pt salt in the water phase, respectively. The SEM images (b and c) show the residual of the catalyst containing BMEs at 700 $^{\circ}$ C after TGA in nitrogen.



Figure S4. a) SEM image and b) and c) TEM images showing the residual of the catalyst containing BMEs at 700 $^{\circ}$ C after TGA in nitrogen. c) shows that the catalyst nanoparticles partly sinter but do not undergo a massive agglomeration after heat treatment. Size increases from 2-4 nm to 5-7 nm.



Figure S5. Raman spectrum of the product of the formation phase, derived from the carbonisation of the BME containing iron catalyst.

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Figure S6. TGA profiles of CNNs decomposition in air for the AOT-system



Figure S7 Carbonised BME not containing metal after synthesis with annealing on carbon paper, silicium, and titanium. No carbon nano-rods could be identified.



Figure S8. SEM images of CNNs produced from platinum nanoparticles with annealing step and respective EDX mapping

Table S1. Weight % composition from EDX mapping.

Ti	5.9
С	82.3
0	6.4
Pt	1.2
Na	2.2
Si	1.9



Figure S9 a) Raman Spectrum for a typical sample of CNNs; b) D/G ratio from Raman spectroscopy for CNNs produced from platinum catalyst



Figure S10. a) Carbon yield as function of catalyst density for CNNs produced from Pt catalyst in Triton-X BME on carbon paper. b) Dimensions of CNNs produced from Pt catalyst in Na-AOT BME on titanium as a function of catalyst concentration and respective SEM images: 12 mM (b-i), 120 mM (b-ii), and 200 mM (b-iii). c) and d) Dimensions of CNNs produced from Fe catalyst 120 mM in Na-AOT BME on titanium as function of c) synthesis temperature and respective SEM images 600 °C (c-i), 650 °C (c-ii), and 700 °C (c-iii); d) ethene flow and respective SEM images: 60ml min⁻¹ (d-i), 96 ml min⁻¹ (d-ii), 120 ml min⁻¹ (d-iii).



Figure S11. SEM images of CNNs grown from different metal: a) cobalt, b) platinum, c) iron



Figure S12. CNNs obtained from TX microemulsions with platinum catalyst and annealing, for different concentrations: a) 30 mM, b) 100 mM, c) 200 mM and different supports: d) Teflon treated carbon paper, e) Carbon paper, f) Carbon black.



Figure S13 SEM images of CNNs grown from iron catalyst 120 mM over different supports: a) carbon paper, b) silicium, c) titanium, d) teflon treated carbon paper, e) unsupported.



Figure S14. Dielectric spectroscopy measurements of CNNs. No extra pressure was applied.

In Figure S13 the electrical conductivity, σ' , and the relative dielectric permittivity, ϵ' , are shown as a function of frequency for a CNN powder that was weakly compressed between two electrodes. The low frequency extrapolated value of the conductivity is equal to the DC-conductivity, about $1.15 \ 10^{-1}$ S/m. Based on the mass of the powder, 60 mg, and the cell dimensions, about $0.27 \ \text{cm}^3$, the effective fill factor is estimated to be 0.1. Using the Clausius-Mossotti relation ² we estimate the conductivity of the CNN material itself to be of the order of 1 S/m which is in the same order of magnitude for similar materials when no pressure is applied.³ However, at higher pressures the conductivity increases which indicates that not all material is participating in the conductivity as calculated here. Nevertheless, it can be concluded that the CNNs are good electrical conductors.

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