

Confinement effects on shape and composition of bimetallic nano-objects in carbon nanotubes

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Electronic Supplementary Information

ESI.1 Materials and methods

Due to the air sensitivity of the magnetic metal precursors, all experiments in which metal precursors were used were performed under inert conditions, either by using Schlenk techniques or in the interior of a glovebox. All the solvents were collected from a solvent purification system (PureSoly MD 7, Innovative Technology, Inc) and subsequently degassed by freeze-pump-thaw three times and finally kept under activated molecular sieves.

[Pt(Me)₂(COD)], [Co{N(SiMe₃)₂}₂(THF)] and [Fe{N(SiMe₃)₂}₂]₂ were furnished by NanoMeps (Toulouse, France). [Pt(acac)₂] (98%) was purchased from STREM Chemicals. Benzylbenzoic acid (97% purity) was purchased from Aldrich. 4-(3-phenylpropyl)pyridine (98%) was purchased from Alfa Aesar. Hexadecylamine was purchased from Aldrich (98%). CNT₁ Pyrograph III, PR-24-XT-PS were furnished by Applied Science, (98% purity, 38 m²g⁻¹) CNT₂ were furnished by Nanocyl, (Nanocyl-3100, 95+% purity, 240 m²g⁻¹)

1. Functionalization of CNTs (CNT₁ and CNT₂)

4g of CNT₁ (Pyrograph III, PR-24-XT-PS furnished by Applied Science, 98% purity, 38 m²g⁻¹) were treated with 170 mL of a HNO₃ solution (69%) at 120°C during 3 hours under magnetic stirring. The black mixture was cooled to room temperature, and then filtered. The black solid was washed with distilled water until pH=6, and dried in an oven at 110°C during 48 hours.

2 g of oxidized CNT₁ were further refluxed in a solution of thionyl chloride (70 mL) for 24 hours at 70°C under Ar. Then the solvent was evaporated under vacuum. Chlorinated CNT₁

were reacted with hexadecylamine (HDA) (2 g, 8.3 mmol) in THF (80 mL) at 70°C for 24 hours. Finally, THF was evaporated and the CNT_{1f} were washed with ethanol (200 mL) to remove excess amine, and dried at 100°C for 24 hours under vacuum.

The CNT_{2f} was prepared with CNT_2 (furnished by Nanocyl, Nanocyl-3100, 95+% purity, 240 m^2g^{-1}) following a similar procedure except that the HNO_3 treatment was carried out at 140°C for 5 hours in the first oxidation step.

2. *Synthesis of the CoPt and FePt NPs*

For the CoPt NPs, 0.2 mmol of 2-benzylbenzoic acid (BBA) (43.6 mg) (Aldrich 97%) was dissolved in 2 mL of toluene, and then this solution was transferred to a Fischer-Porter tube. 0.1 mmol of $[\text{Pt}(\text{CH}_3)_2(\text{COD})]$ (33.3 mg) was dissolved in 1.5 mL of toluene, and then the Pt solution was added dropwise (1.5 mL in 2 min) to the Fischer-Porter tube under stirring. After 5 min, a solution of 0.2 mmol of 4-(3-phenylpropyl)pyridine (PPP) (40.2 mg) (Alfa Aesar, 98%) in 1.5 mL of toluene was added rapidly. After 5 min, a solution of 0.084 mmol of $[\text{Co}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})]$ (38 mg) in 1.5 mL of toluene was added dropwise (1.5 mL in 2 min) into the tube under stirring. The starting solution was charged with 3 bar H_2 and then heated at 100°C for 24 hours. The CoPt NPs were isolated from the as-synthesized colloidal solution by adding 10 mL of pentane, and then the supernatant was removed. The precipitate was washed with 10 mL of pentane 3 times. The black powder was dried and kept in a glove-box.

The synthesis of FePt NPs was performed following the same procedure except using the Fe precursor $[\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (37.7 mg, 0.05 mmol).

3. *In situ decomposition of the starting solution in the presence of the functionalized CNTs*

The starting solution, consisting of the Co or Fe precursor and the aromatic ligands (BBA and PPP) in toluene, was prepared as described in the previous section, and then was transferred to another Fischer-Porter tube, containing a suspension of the functionalized CNTs (30 mg of CNT_{1f} or CNT_{2f}) in 3 mL of toluene. The colloidal mixture was charged with 3 bar of H_2 following a thermal reduction at 100°C for 24 hours.

For the CoPt* the same procedure as above was used, except for the Pt precursor which was $[\text{Pt}(\text{acac})_2]$ and the $[\text{Co}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})]$ amount which was 0.1 mmol.

For the FePt* the same procedure was used except for the Pt precursor which was $[\text{Pt}(\text{acac})_2]$.

The CNT-confined bimetallic nano-objects were isolated from the ultimate colloidal solution by decanting and removing the supernatant. The precipitate was then washed with 10 ml of toluene 3 times and pentane 3 times. Finally, the black powder was dried and kept in a glove-box.

Conventional TEM characterization was performed with a JEOL JEM 1400 microscope equipped with LaB₆ thermionic electron source and working at an acceleration voltage of 120 kV.

HRTEM and EDS spectra of small NPs analysis were performed using JEOL JEM 2100F equipped with a field emission gun (FEG) and a SDD Bruker EDS detector, working at 200 kV.

STEM-EDS analyses were performed in a Philips CM20 FEG equipped with a field emission gun (FEG) and a SDD Bruker EDS detector working at 200 kV.

XRD were carried out on samples enclosed by two Kapton foils in a PANalytical Empyrean, using the Co K α radiation (K α Wavelength (λ) = 1.789 Å).

ESI.2 TEM of bimetallic CoPt and FePt free nanoparticles

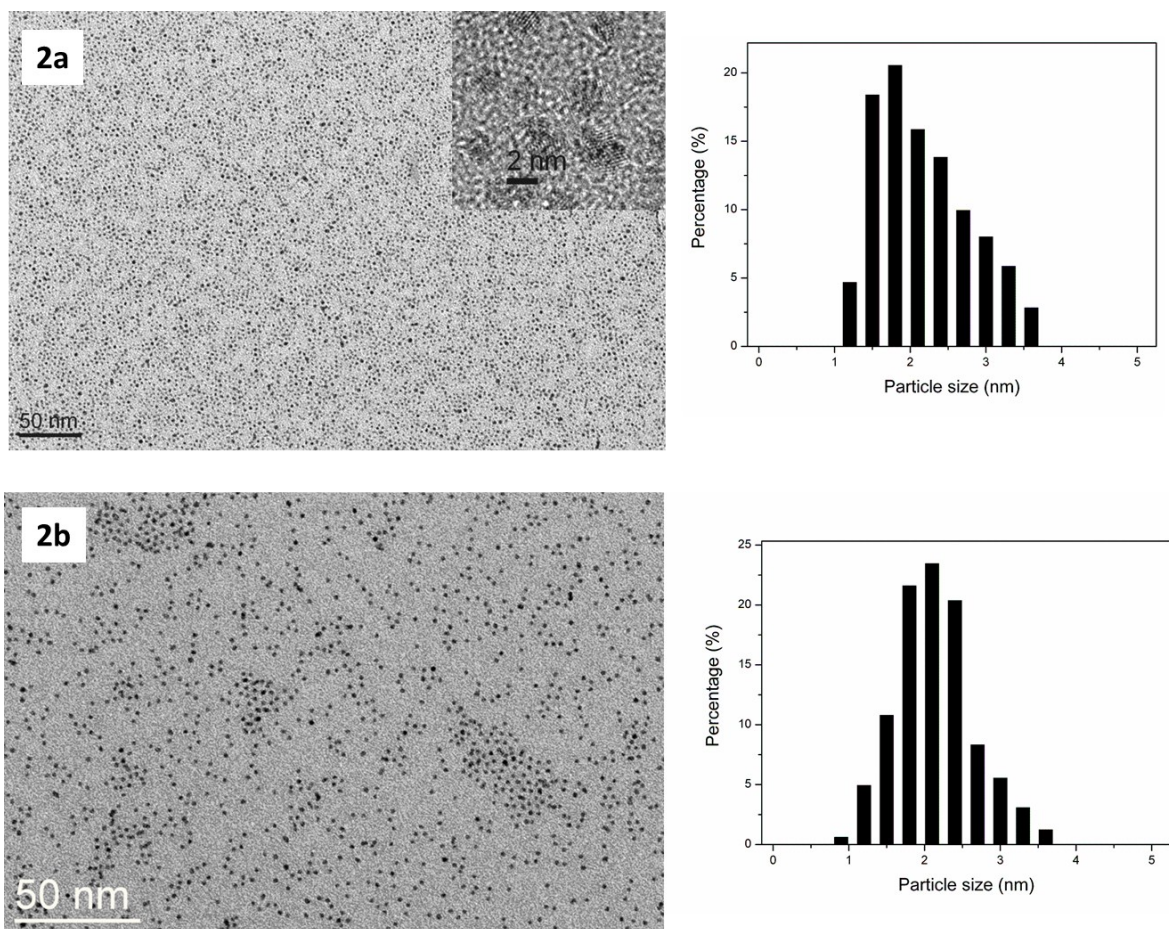


Figure ESI.2 a) Free CoPt NPs ($d = 2.0 \pm 0.6$ nm), scale bar = 50 nm, inset HRTEM scale bar = 2 nm; b) FePt NPs ($d = 2.0 \pm 0.5$ nm), scale bar = 50 nm.

ESI.3 TEM of empty carbon nanotubes

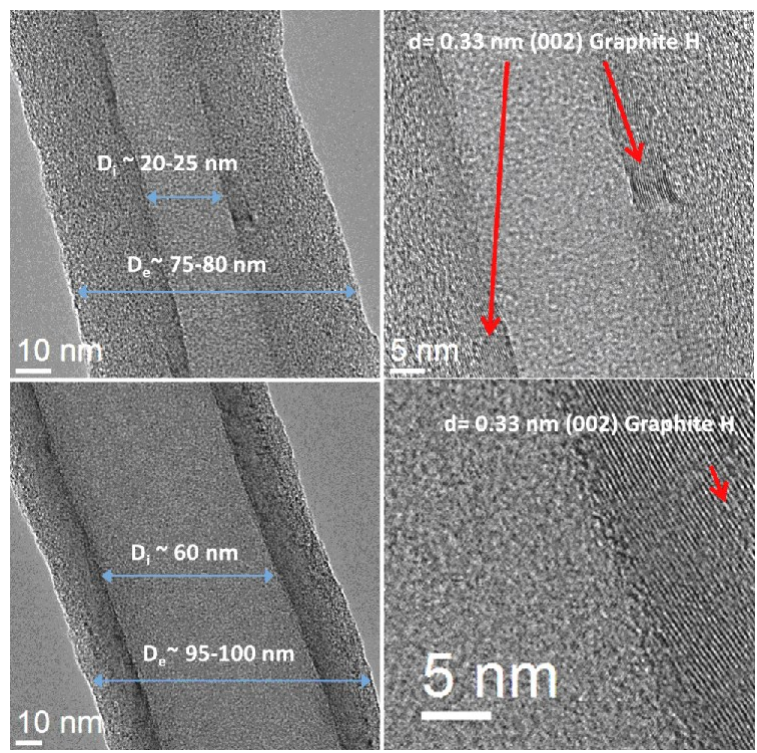


Figure ESI.3a TEM micrographs of **CNT₁**

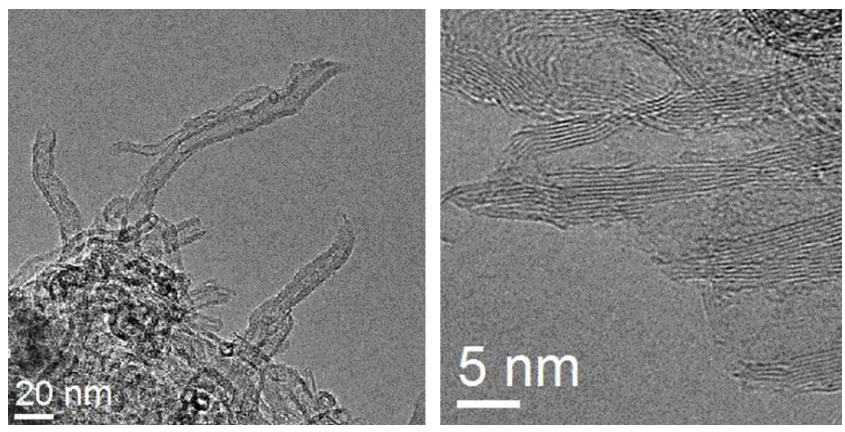


Figure ESI.3b TEM micrographs of **CNT₂**

ESI.4 Supplementary TEM of filled CNTs

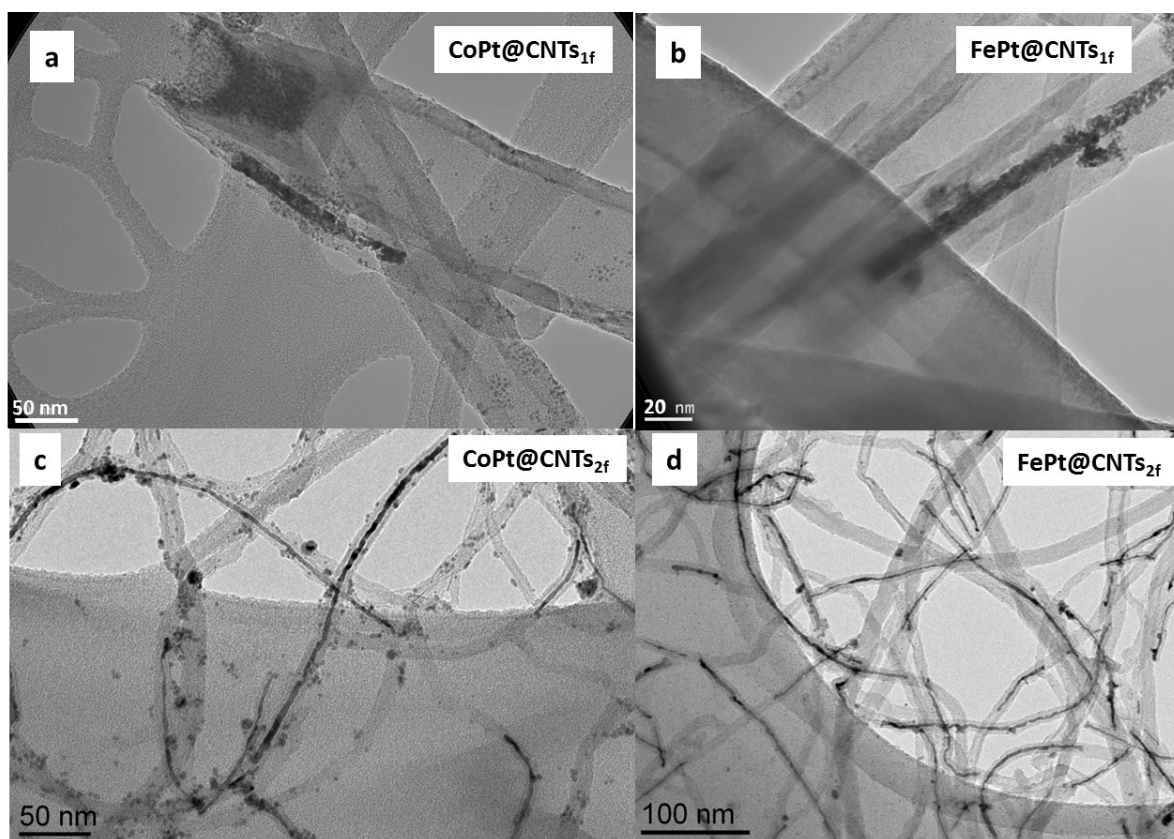


Figure ESI4. a) CoPt@CNTs_{1f}; scale bar= 50 nm b) FePt@CNTs_{1f}; scale bar = 20 nm c) CoPt@CNTs_{2f}; scale bar= 50 nm d) FePt@CNTs_{2f}; scale bar= 100 nm

ESI.5: X-ray diffraction of NWs@CNTs

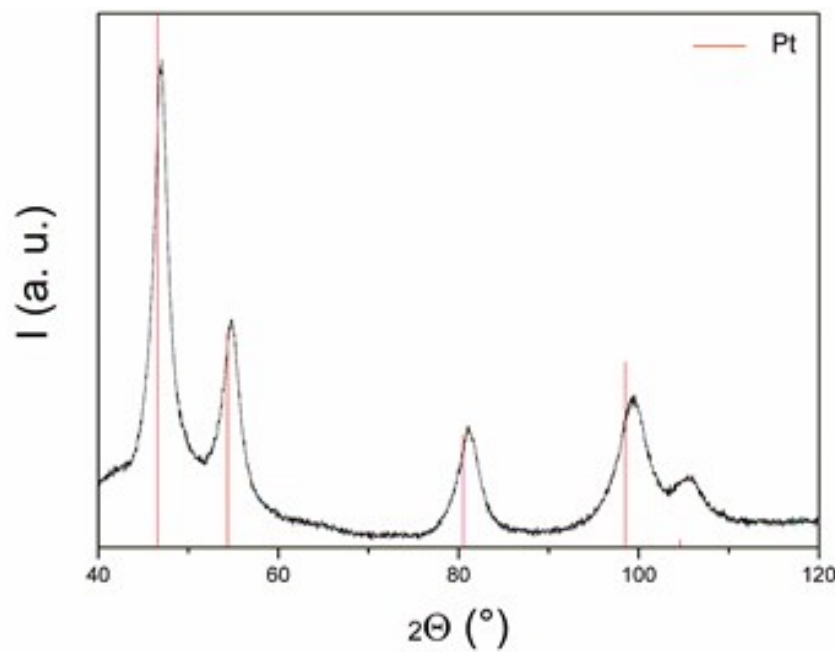


Figure ESI.5a: XRD of CoPt nanowires confined in CNT_{2f}

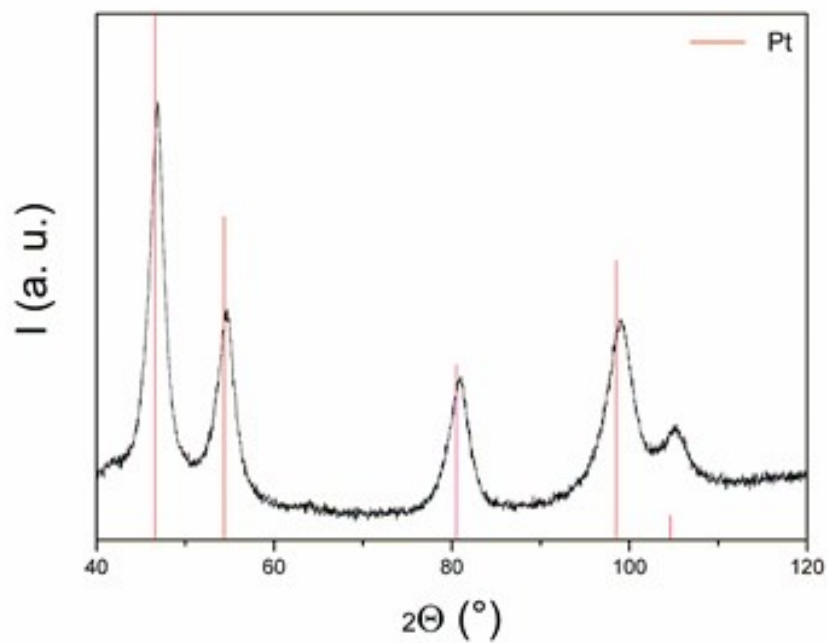


Figure ESI.5b: XRD of FePt nanowires confined in CNT_{2f}

SI.6 Coalesced FePt* NPs confined within CNT_{2f}

