Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary information

In situ observations of Pt nanoparticles coalescing inside carbon nanotubes

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Methods.

For the synthesis of platinum filled carbon nanotubes a platinum (II) acetylacetonate ($Pt(acac)_2$) served as the precursor. $Pt(II)(acac)_2$ and commercial multiwall carbon nanotubes (XinNano Materials Inc, China) were placed into a quartz tube in which one end was sealed. The other end was mounted on to a high vacuum unit and the tube then evacuated to 10^{-6} mbar. The dynamic vacuum was then closed off by means of a valve and the open end of the tube was sealed using a propane/butane/oxygen flame. The sealed quartz tube was then heated in an oven at 200°C for 3 days. During this process the platinum (II) acetylacetonate vapour can decompose forming Pt nanoparticles on the surface of the CNT aswell as filling of the CNT with Pt through capillary action.

A small amount of the as-produced material was then pressed onto a Cu-lacey carbon TEM grid. The sample was characterized with a JEOL JEM-2010F transmission electron microscope (TEM) retrofitted with two CEOS third-order spherical aberration correctors for the objective lens (CETCOR) and the condenser system (CESCOR). The microscope was operated using an electron acceleration voltage of 80 kV. The temperature in the microscopes column was at room temperature.

Supplementary results.

S1. Statistics

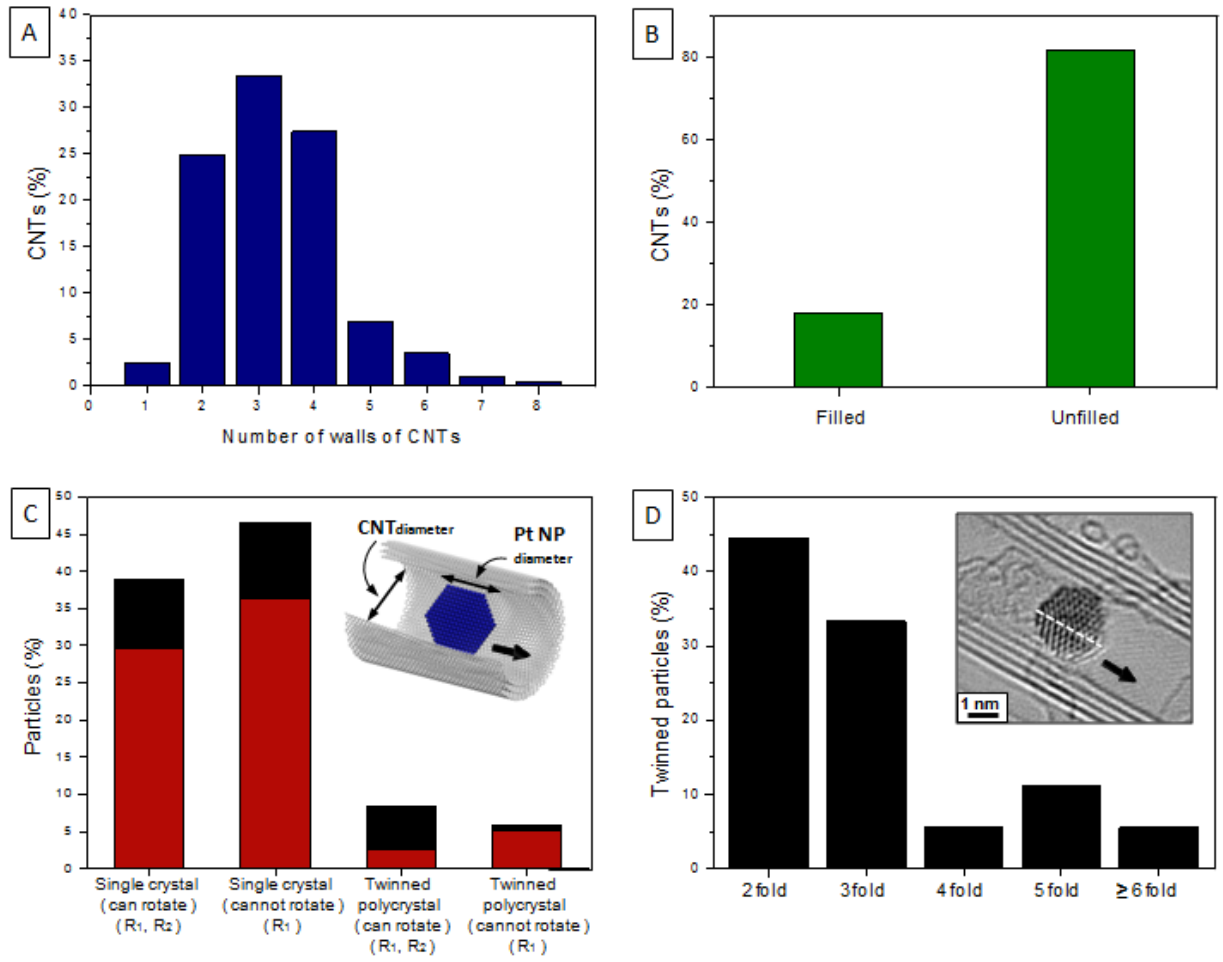

Fig. S1. (A) Statistics on the number of walls of the CNT as determined from TEM images. (B) The percentage amount of filled and unfilled CNTs. (C) Statistics on the fraction of NPs with their (111) plane parallel to the CNT walls (red colour – see inset). The fraction with other orientations or rotated (111) planes is shown in black. (D) As for (C) but for polycrystalline particles with twinning. The white dashed line shows twinning plane.

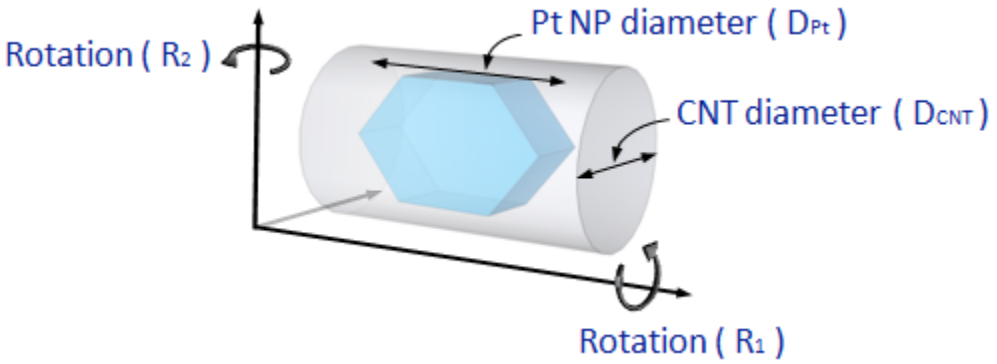

Fig. S2. Schematic of a platinum nanoparticle inside a carbon nanotube. R_1 and R_2 are rotations which are allowed for the nanoparticles.

If D_{CNT}/D_{Pt} is less or equal to 0.9 then rotation R_2 is forbidden and rotation R_1 is allowed. When D_{CNT}/D_{Pt} is greater or equal to 0.9 then rotation R_2 and R_1 are allowed.

S2. Calibration

To calibrate d-spacing for platinum nanoparticles was used the interlayer distance between walls in the CNTs graphite (ca.0.35 nm). A line profile was generated to measure the spacing of the atomic planes. Then the distance was divided by the total number of peaks.

S3. Detailed coalescence process

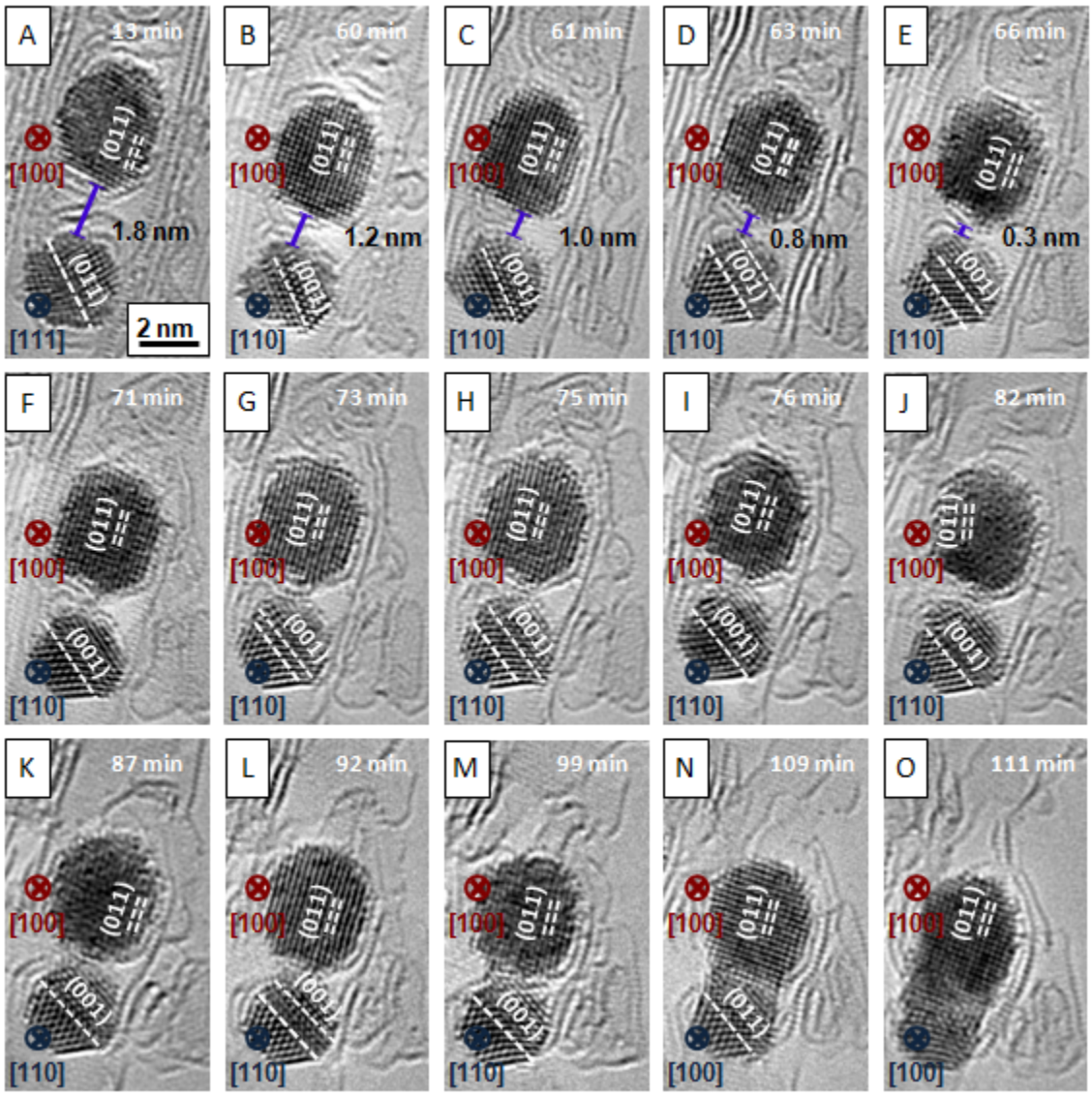

Fig. S4. Detailed in situ coalescence process of platinum particles.

S4. EDS spectrum

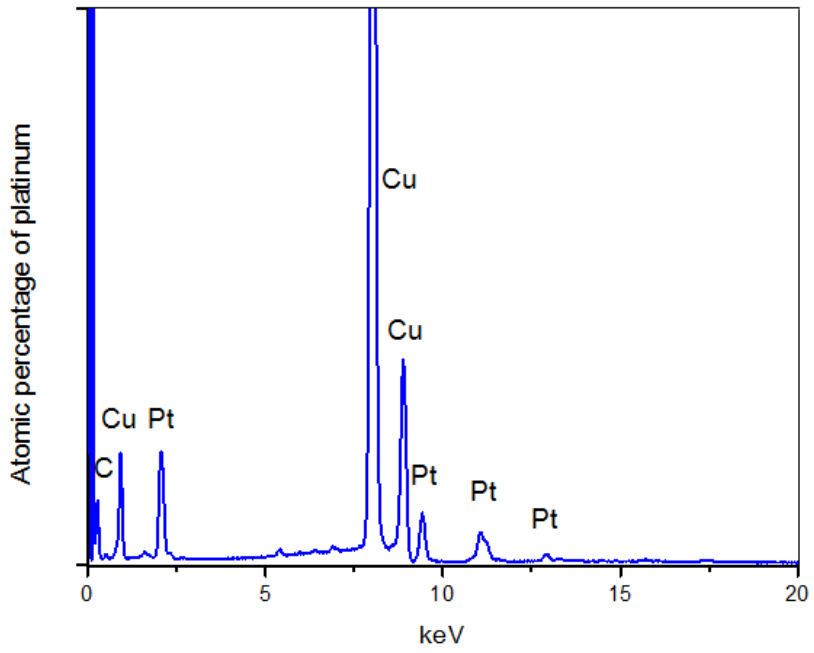

Fig. S5. EDS spectrum of the platinum filled carbon nanotubes.

The composition of the as-produced material was checked by energy dispersive X-ray Spectroscopy (EDS). The Cu signals are from the Cu TEM.

S5. Temperature rise calculations.

Liu et al. studied the heating effect experienced by glass-embedded CdS nanocrystals under continuous electron bombardment [1]. In their work they came up with the following approximation to calculate the temperature rise in a nanoparticle (ΔT_e) due to beam heating:

$$\Delta T_e \approx \frac{3JQ}{8\kappa e} R_{Pt}^2 log(1 + \frac{4\kappa t_e}{cdR_{Pt}^2}) \quad \ldots(1)$$

Where J is the current density, R_{Pt} is the nanoparticle's radius (a platinum nanoparticle, in our case), κ is the thermal conductivity, e is the electron charge, t_e is the irradiation time, c is the specific heat and d is the material's density. The parameter Q is the total energy loss of an electron travelling through the specimen. Q can be thought of as the sum of the energy loss due to direct collisions between the incoming electrons and the nuclei in the material (Q_c) and the energy loss due to excitations of the atomic electrons by the beam electrons (Q_e). Calculation of Q_c and Q_e requires knowledge of the beam parameters and the

specimen's properties, however, Pages et al. have computed electronic energy loss values for a multitude of materials at different beam energies and provide a very complete set of tables with their results [3].

We can then plug in the appropriate values for κ, c and d for a platinum nanoparticle with a radius of 3 nm and the energy loss Q for a Pt target being irradiated by an 80 kV electron beam (taken from Pages's tables) in equation (1). Thus, considering an irradiation time of 100 seconds we get a temperature rise ΔT_e < 1K in the Pt nanoparticle.

Liu et al [1] have given a formula on how to calculate the temperature rise (ΔT_e) of any system under electron beam irradiation due to electron excitations, Coulomb encounter energies, electron beam parameters (energy and current density) and the matrix parameters Furthermore when the energetic electrons pass through the nanomaterial matrix, they create thermal spikes The energy loss occurs mainly via two processes: (a) from electron excitations (Q_e) and (b) Coulomb encounter with nuclei (Q_c) as shown in the following equations.

$$Q_e = Q[\log\left(\frac{m^2C^4\beta^2}{Z^2I^2(1-\beta)^2}\right) - \beta^2 + 0.198] \quad (1)$$

$$Q_c = \frac{Q}{1837.5A} log(\frac{T_m}{T_a}) \quad (2)$$

where $Q = 2\pi n Z_2 r_e^2 m_c^2/\beta^2$, $T_m = (560.8)/A)X(X+2)$, $X = E_p/m_c^2 = 0.2$ MeV/0.511 = 0.391, $\beta = v/c$, Z = 78 for platinum (Pt), $r_e = 2.818 \cdot 10^{-15}$ m (classical electron radius), Rh = 13.6 eV (Rydberg energy for hydrogen atom), A = 195 (atomic mass for Pt), n is the number density of atoms in the particle, IZ = 13.54 eV (the average ionization potential for Pt atom) . The total thermal energy obtained by the matrix can be shown as $Q = Q_e + Q_c$ which leads to rise in rise temperature [2].

The temperature rise (ΔT_e) of Pt nanoparticles caused by electron beam irradiation was estimated from equation [3]:

$$\Delta T_e \approx \frac{3JQ}{8\kappa e} R_{Pt}^2 log(1 + \frac{4\kappa t_e}{cdR_{Pt}^2}) \quad (3)$$

Where J is the electron beam current density passing through the Pt nanoparticle, Q – the electron energy loss by irradiation through the Pt nanoparticle and was obtained from the values in the tables of Pages et.

al [4], κ – the thermal conductivity of platinum, e – the electron charge, R_{Pt} – the radius of the Pt nanoparticle , t – irradiation time, c – specific heat of Pt, d – density of platinum. We calculate ΔT_e from eq. (3) considering a long irradiation time of 100 s. The result showed $\Delta T < 1K$.

Movie 1. In situ TEM movie of coalescing Pt particles (corresponding to Fig. 4 and Fig. S4).

References:

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3 L. Pages, E. Bertel, H. Joffre and L. Sklavenitis, *Atomic Data*, 1972, **4**, 1-127;