

Encapsulation of Discrete Gold Nanoparticles in Carbon Nanotubes

*Alessandro La Torre,^a Graham A. Rance,^a Jaouad El Harfi,^a Jianing Li,^a Derek J. Irvine,^a Paul D. Brown^b
and Andrei N. Khlobystov^{a*}*

Supporting Information

S.1 TEM micrograph showing different stages of nanotube filling with Au-NP

These micrographs illustrate different stages of nanotube filling as shown in Scheme 2 in the main text. Gold nanoparticles are initially adsorbed on MWNT surface (Figure S1a). Under the scCO₂ conditions at 100 °C nanoparticles undergo Ostwald ripening, so that the total number of Au-NP decreases as the average nanoparticle diameter increases (Figures S1b and S1c show intermediate stages of nanotube filling for samples exposed to scCO₂ for 1 hour). Nanoparticles with diameters below the snug fit enter nanotubes reversibly (Figure 1Sb). But once their diameters reach the snug fit diameter for a particular nanotube (Figure 1Sd) the encapsulation becomes irreversible.

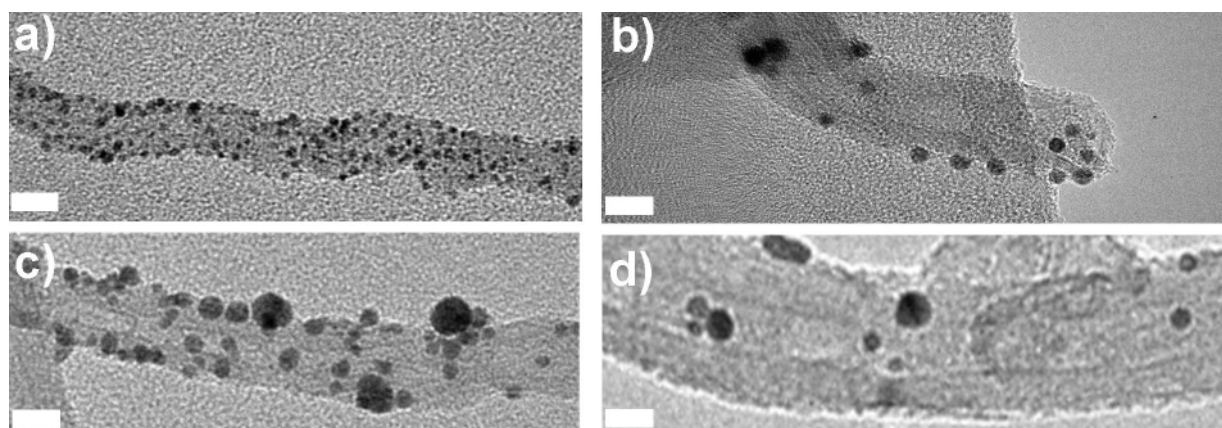


Figure S.1. Bright field transmission electron micrographs of carbon nanotubes and gold nanoparticles: (a) Au-NP deposited on MWNT before, (b, c) one hour after and (d) 24 hours after treatment with scCO₂. Scale bars are 10 nm.

S.2. Characterisation of multiwall carbon nanotubes by transmission electron microscopy

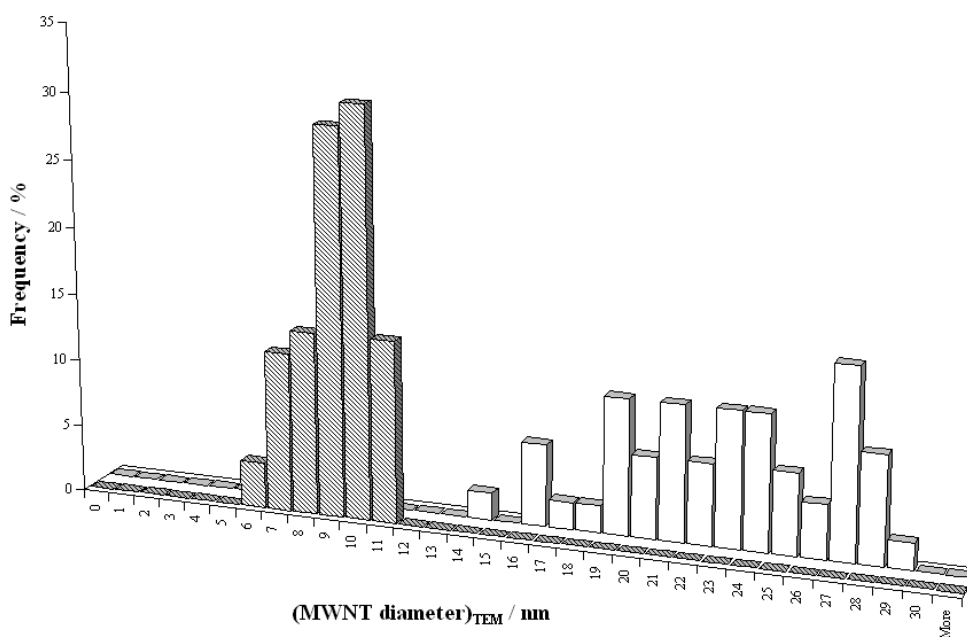


Figure S.2. Statistical analysis of the internal (grey) and external (white) diameters of the CVD grown multiwall carbon nanotubes, assessed using TEM. Internal diameter = 8.7 ± 1.3 nm (5.2 – 11.0 nm, N = 50). External diameter = 22.4 ± 3.8 nm (14.0 – 29.0 nm, N = 50).

S.3. Synthesis and characterisation of alkanethiolate-stabilised silver nanoparticles

The synthesis of dodecanethiolate-stabilised silver nanoparticles was performed using the monophasic protocol described by Kang and Kim.¹⁹ Decanethiol (0.4 mmol) was added to a solution of silver nitrate (0.9 mmol) in ethanol (30 mL) and the mixture was stirred vigorously for 10 min at room temperature. A saturated solution of sodium borohydride in ethanol (60 mL) was then added and the resulting mixture stirred vigorously for 2 hr at room temperature. The product was precipitated from solution by the further addition of ethanol (350 mL) before storing at -30°C for 24 hr. The precipitate was then filtered using a $0.45\ \mu\text{m}$ pore size polytetrafluoroethylene (PTFE) membrane filter and washed with ethanol (250 mL) and acetone (250 mL) before final drying under vacuum to yield a black solid (180 mg).

UV-vis (cyclohexane): λ/nm 450 ($\epsilon = 4.6 \times 10^7\ \text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}$).

DLS (cyclohexane): Average Particle Diameter / nm 9.1 ± 3.1 (4.9 – 28.2 nm, Polydispersity Index = 0.27, N = 5).

TEM (100 kV, holey carbon film): APD/nm 7.4 ± 0.7 (6.0 – 9.7 nm, N = 117).

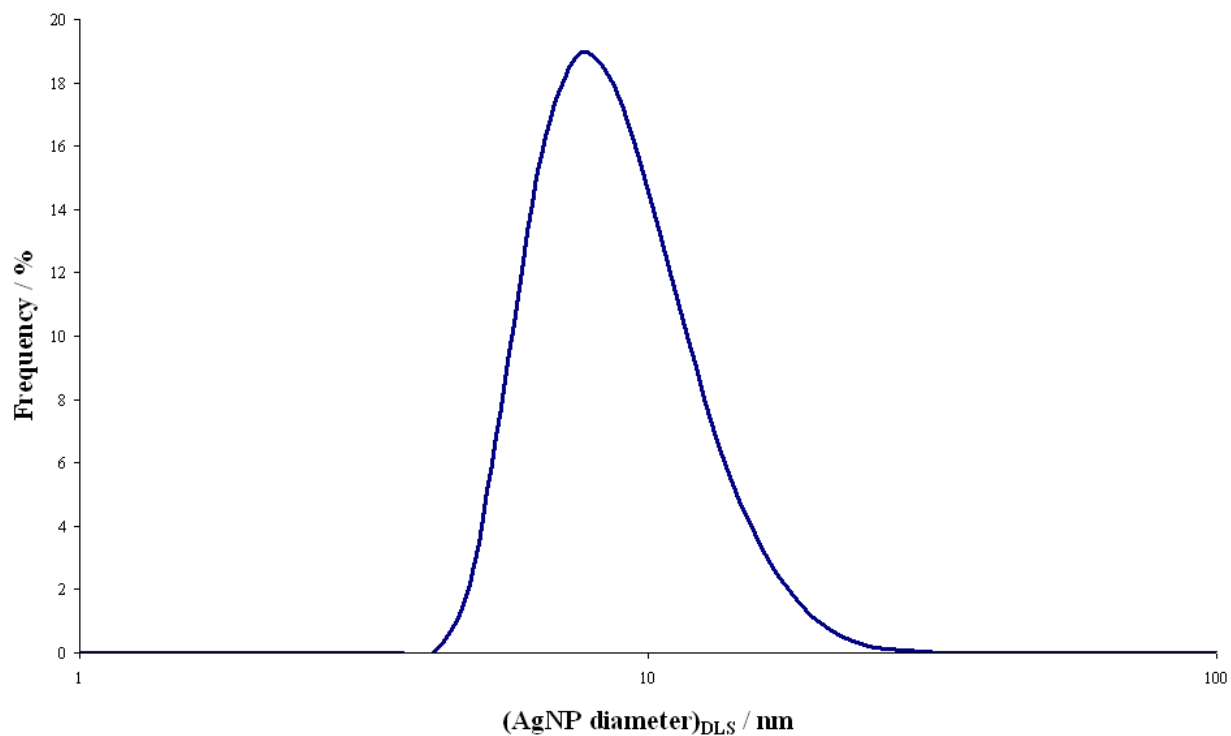


Figure S.3.1. Size distribution of silver nanoparticles, assessed using DLS. Diameter = 9.1 ± 3.1 nm (4.9 – 28.2 nm, PdI = 0.27, N = 5).

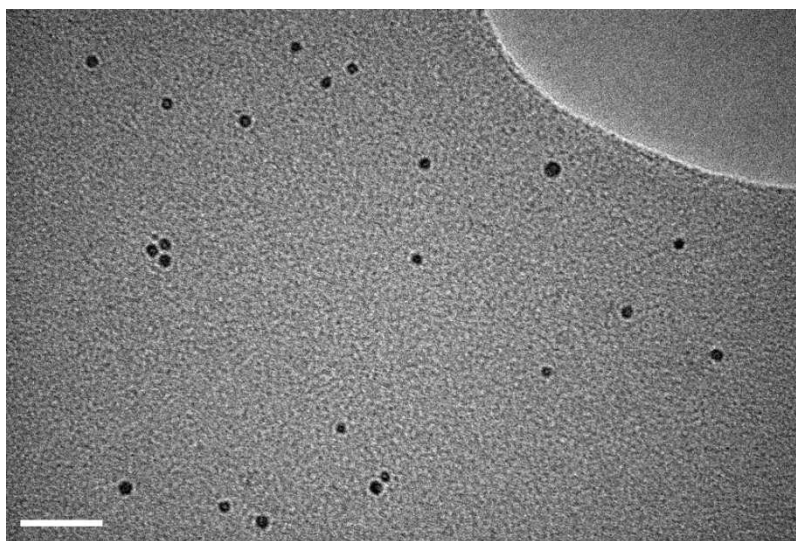


Figure S.3.2. Bright field TEM images of dodecanethiolate-stabilised silver nanoparticles. The scale bar is 50nm.

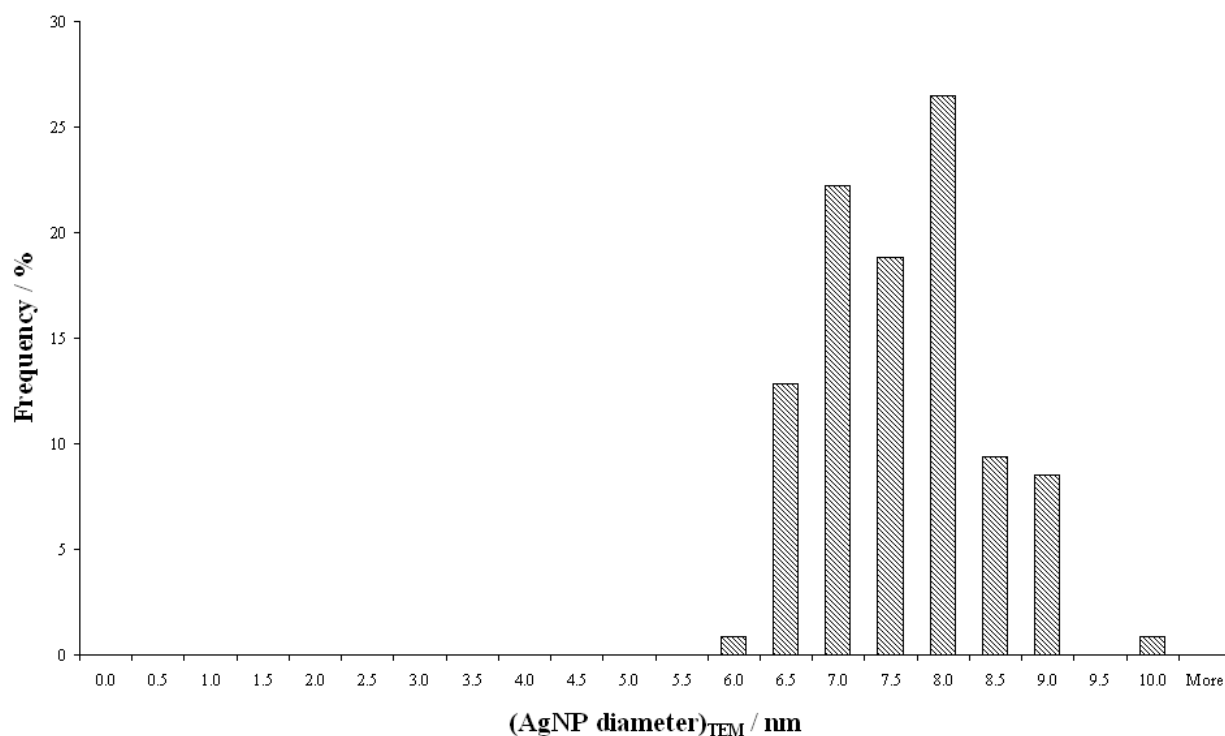


Figure S.3.3. Size analysis distribution of silver nanoparticles, assessed using TEM. Diameter = 7.4 ± 0.7 nm (6.0 – 9.7 nm, N = 117).

S.4. Preparation of short, open carbon nanotubes via oxidative cutting

Multiwall carbon nanotubes (10 mg, TimesNano, purified) were added to a solution of dodecanethiolate-stabilised silver nanoparticles (3 mg) in cyclohexane (10 mL) and the resulting black suspension sonicated for 30 min at room temperature. This was then filtered using a 0.45 μ m pore size PTFE membrane filter and washed with cyclohexane (3 x 50 mL) and acetone (50 mL) before final drying under vacuum to yield a black solid (12 mg). The product was then placed in an alumina crucible and heated in air at 380 °C for 25 min to yield a black solid (6 mg). This was then added to nitric acid (2 M, 10 mL) and the resulting black suspension sonicated for 30 min at room temperature. The resulting product was then diluted with deionised water (20 mL), filtered using a 0.45 μ m pore size PTFE membrane filter, washed with ethanol (50 mL) and acetone (50 mL) and dried under vacuum to yield a black solid (5 mg). This product was then placed in an alumina crucible and heated in air at 300 °C for 10 min to yield a black solid (5 mg).

TEM (100 kV, holey carbon film): 324 ± 140 nm (range 300 nm, count 100).

S.5. Synthesis and characterisation of alkanethiolate-stabilised gold nanoparticles

The synthesis of dodecanethiolate-stabilised gold nanoparticles was performed using a modified Brust-Schiffrin protocol.¹⁷ A solution containing tetraoctylammonium bromide (0.4 mmol) in toluene (60 mL) was added to an aqueous solution of tetrachloroauric acid trihydrate (0.2 mmol) in deionised water (30 mL) and the mixture stirred vigorously for 10 min at room temperature. A solution containing dodecanethiol (0.2 mmol) in toluene (10 mL) was then added and the resulting mixture stirred vigorously for 10 min at room

temperature. A further solution containing sodium borohydride (2.0 mmol) in deionised water (30 mL) was then added and the resulting mixture stirred vigorously for 20 hr at room temperature. The biphasic mixture then was separated and the retained organic layer was washed with water (3 x 100 mL) and dried over anhydrous sodium sulphate. The resulting product was further purified by gentle centrifugation (5,000 x g, 10 min). The supernatant was removed and concentrated (\approx 5 mL) under vacuum. The product was then precipitated from solution following the addition of ethanol (350 mL) and stored at -30 °C for 24 hr. The resulting precipitate was then filtered using a 0.45 μ m pore size PTFE membrane filter, washed with ethanol (250 mL) and acetone (250 mL) and then dried under vacuum to yield a brown solid (38 mg).

UV-vis (toluene): λ /nm 515 ($\epsilon = 6.0 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$).

DLS (toluene): Average Particle diameter/nm 3.2 ± 0.7 (2.0 – 5.6 nm, PdI = 0.28, N = 5).

TEM (100 kV, continuous carbon film): Average Particle Diameter/nm 2.3 ± 0.4 (1.3 – 3.3 nm, N = 200).

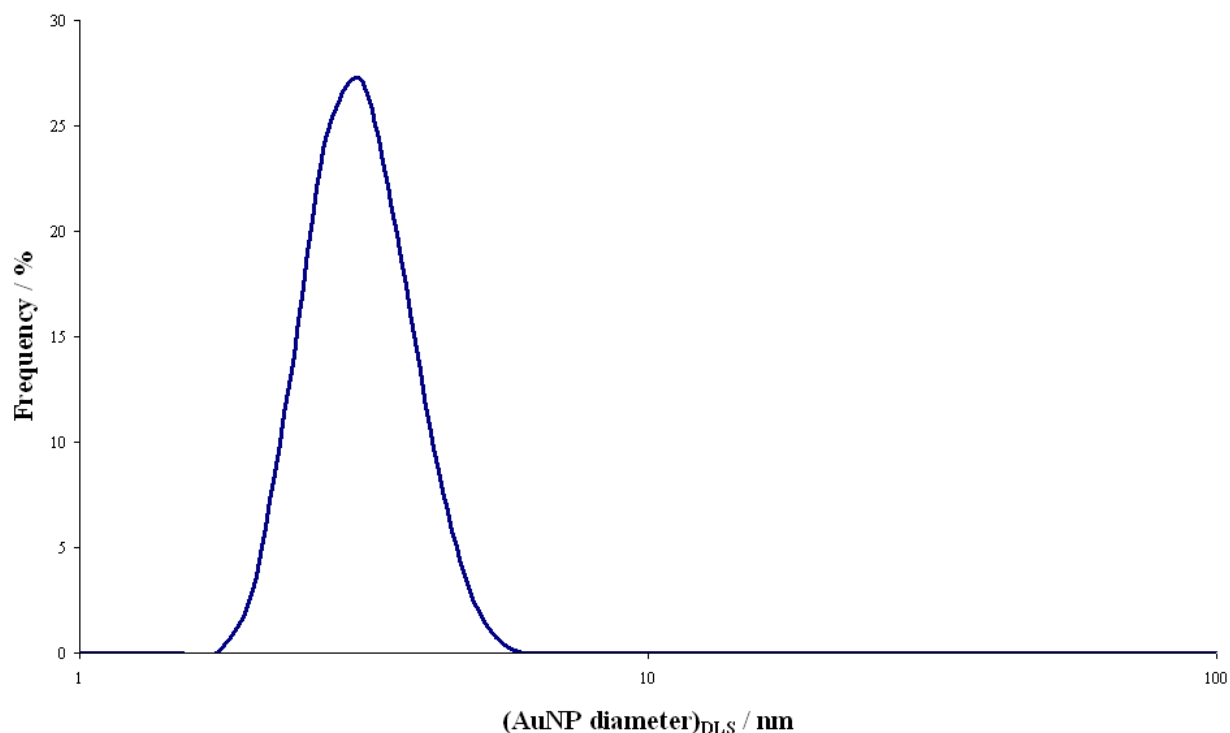


Figure S.5.1. Size of gold nanoparticles, assessed using DLS. Diameter = 3.2 ± 0.7 nm (2.0 – 5.6 nm, PdI = 0.28, N = 5).

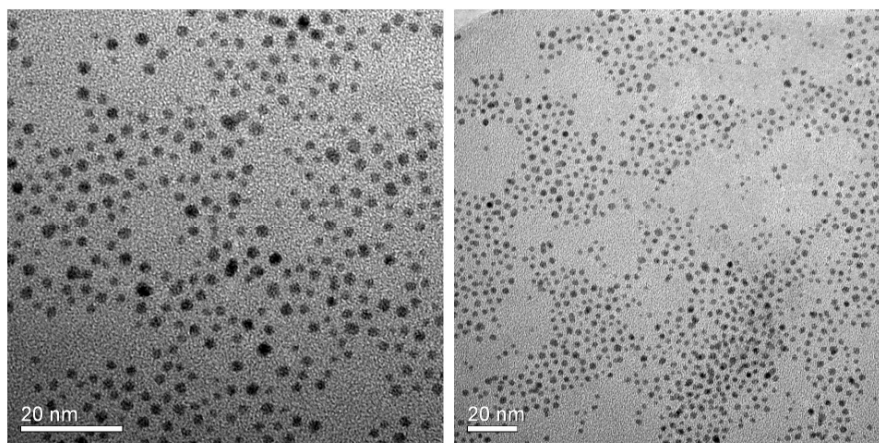


Figure S.5.2. Bright field TEM images of dodecanethiolate-stabilised gold nanoparticles.

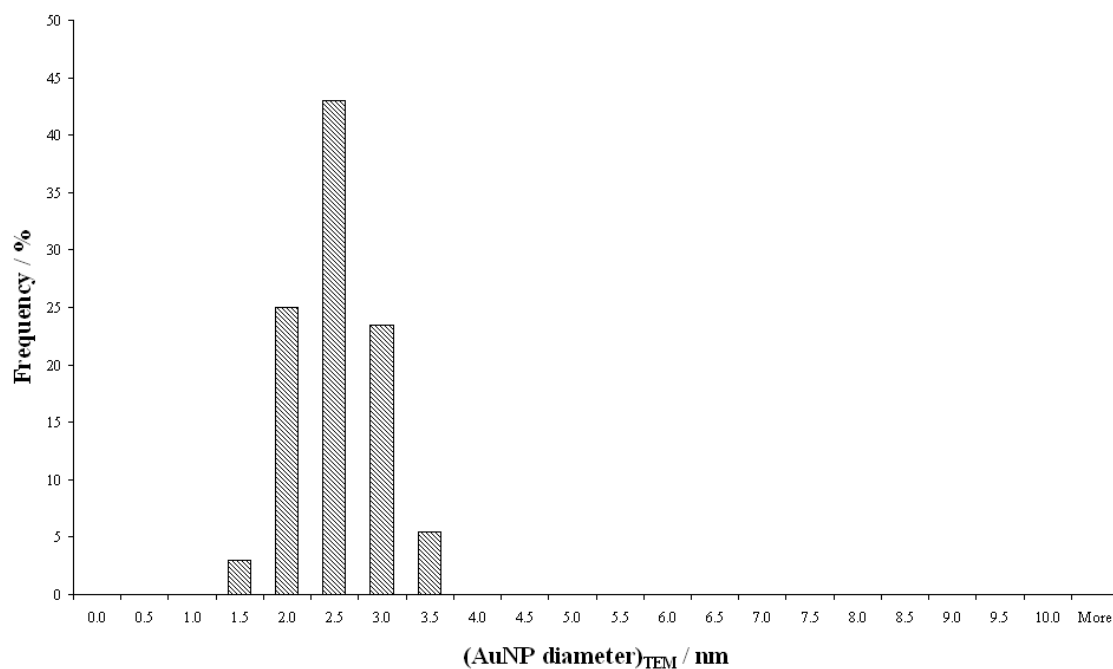


Figure S.5.3. Size of gold nanoparticles, assessed using TEM. Diameter = 2.3 ± 0.4 nm (1.3 – 3.3 nm, N = 200).

S.6. *Encapsulation of gold nanoparticles in carbon nanotubes*

Multiwall carbon nanotubes (2 mg, TimesNano, short and open) were added to a solution of dodecanethiolate-stabilised gold nanoparticles (8 mg) in hexane (10 mL) and the resulting black suspension transferred into an autoclave and mixed with carbon dioxide (100 °C, 4000 psi) for 24 hr. The resulting black solid was then extracted with hexane and filtered using a 0.45 µm pore size PTFE membrane.

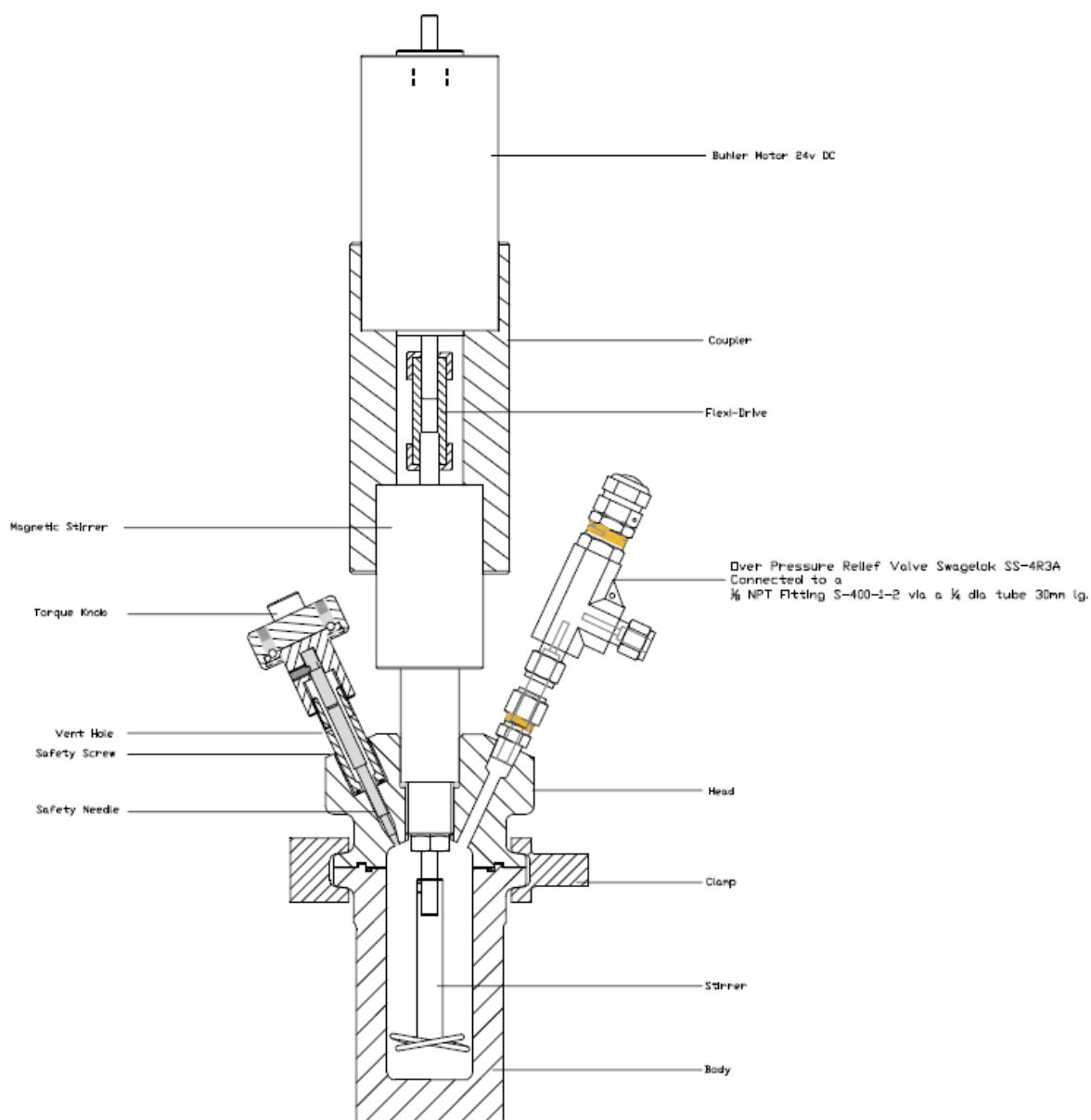


Figure S6.1. Schematic diagram of high pressure autoclave used for scCO₂ experiments.

S.7. Intermediate stage of scCO₂ treatment

Multiwall carbon nanotubes (2 mg, TimesNano, shorted and open) were added to a solution of dodecanethiolate-stabilised gold nanoparticles (8 mg) in hexane (10 mL) and the resulting black suspension transferred into an autoclave and mixed with carbon dioxide (100 °C, 4000 psi) for 1 hr. The resulting black solid was then extracted with hexane and filtered using a 0.45 µm pore size PTFE membrane.

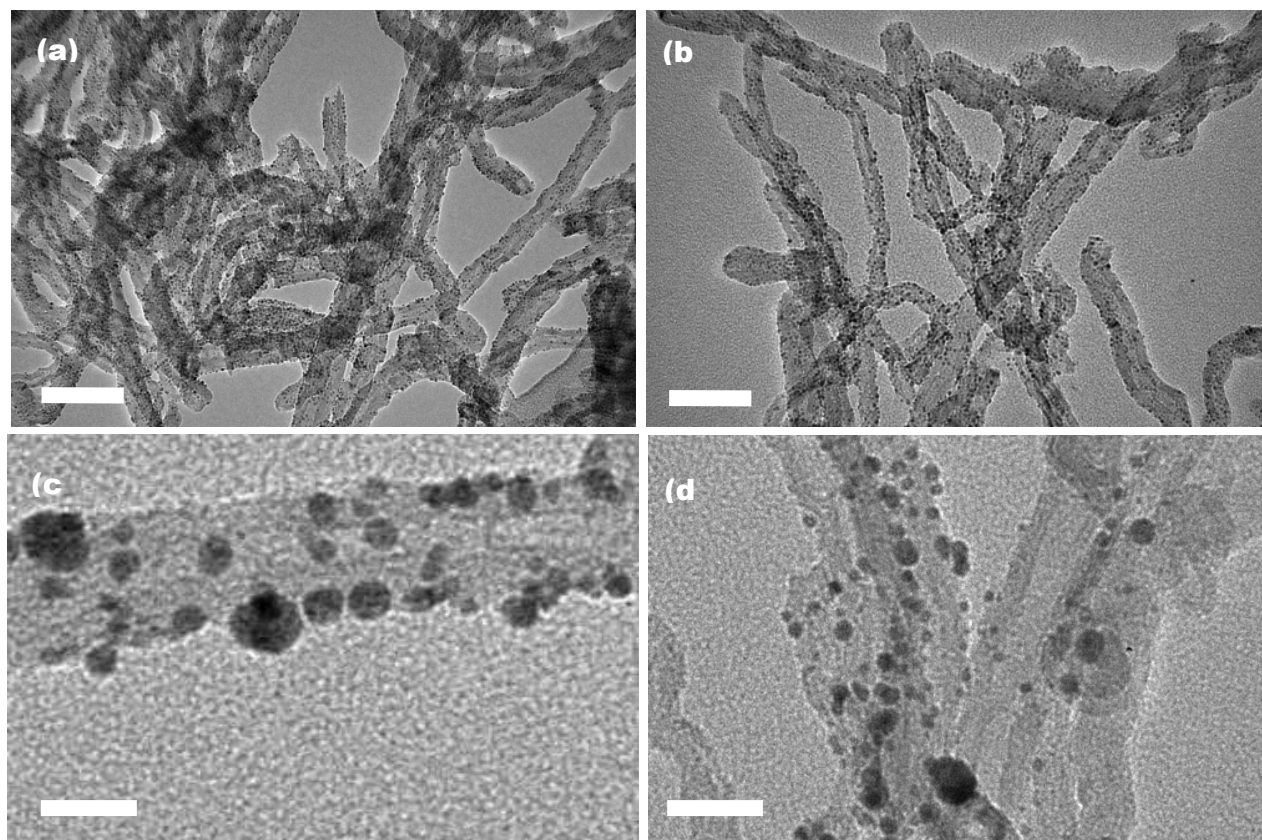


Figure S.7.1. (a-b) TEM images of MWNT AU-NP composite material before scCO₂ treatment scale bars 50 nm. (c-d) TEM images of MWNT AU-NP composite material after 1 hr scCO₂ treatment scale bar 20 nm

TEM images (Figure S.7.1) clearly illustrate that AuNP undergo Ostwald ripening on nanotube surfaces on the timescale of hours. The ripening is typically complete after 24 h exposure to scCO₂.

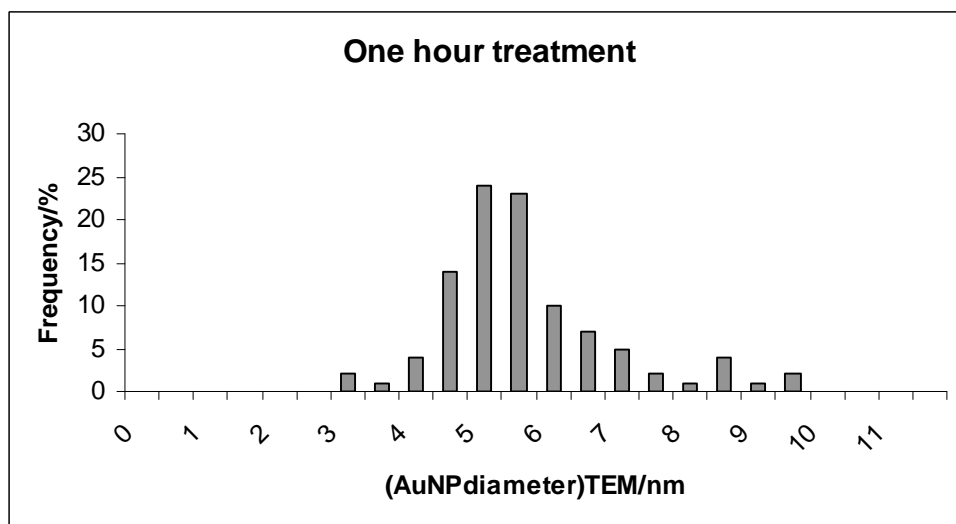
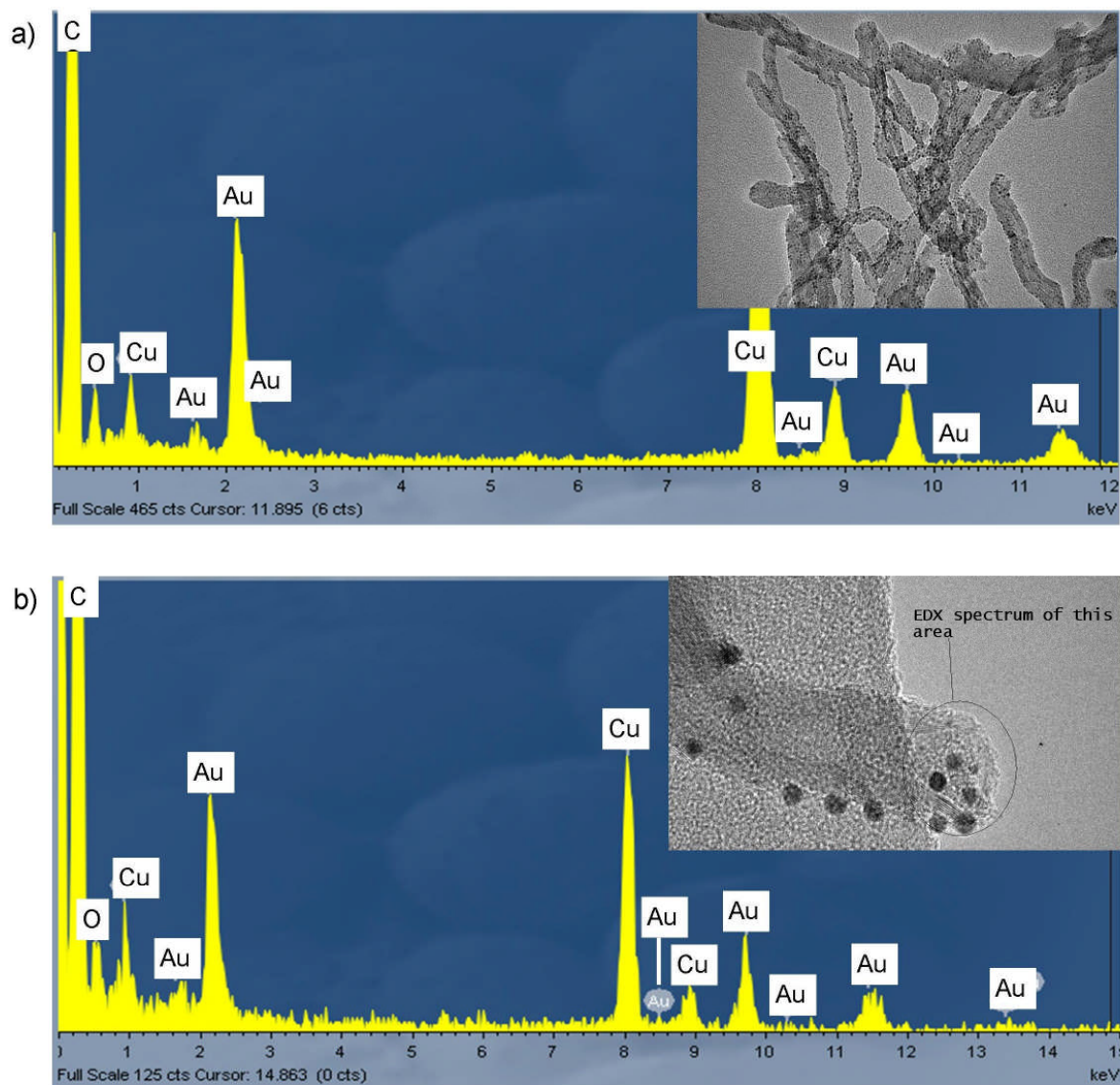


Figure S.7.2 Size analysis distribution of gold nanoparticles, after one hour of scCO₂ treatment, assessed using TEM. Average diameter = 5.4 ± 0.9 nm (range 3.0 – 9.5 nm, N = 100).

S.8. EDX Analysis

To confirm the chemical identity of nanoparticles encapsulated and adsorbed on nanotubes after the treatment with $scCO_2$, energy dispersive X-ray (EDX) spectroscopy was carried



out.

Figure

S.8. TEM images and EDX spectra corresponding to selected areas for samples of MWNT/Au-NP composite material (a) before and (b) one hour after treatment with $scCO_2$.

EDX spectroscopy shows no presence of residual AgNP used for cutting of nanotubes, and the composition of all nanoparticles observed inside or on the surface of MWNT was confirmed to be metallic gold. Copper peaks are due to a TEM copper grid supporting the specimen.