Supporting information

Nanoparticle-Nanotube Interactions in Solution: the Effect of pH and Ionic Strength

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S.1.   *Preparation of materials*

Synthesis and characterisation of citrate-stabilised gold nanoparticles (AuNP)

Citrate-stabilised gold nanoparticles were prepared by modification of the method outlined by Slot and Geuze.[18] An aqueous solution of tetrachloroauric acid trihydrate (1.00 mL of a 1 % wt. aqueous stock solution, 0.026 mmol) in deionised water (79.00 mL) was heated to 60 ^{o}C with stirring. To this was added a separate solution heated to 60 ^{o}C containing trisodium citrate dihydrate (4.00 mL of a 1 % wt. aqueous stock solution, 0.136 mmol) and tannic acid (0.01 mL of a 1 % wt. aqueous stock solution, 29.4 μmol) in deionised water (3.99 mL) and the combined solution heated at 60 ^{o}C until a ruby red colour was observed. This was rapidly brought to the boil and finally cooled to yield a ruby red solution of citrate-stabilised gold nanoparticles.

UV-vis (H$_2$O): λ/nm 521.32 (6.09x10^8).

DLS (H$_2$O): APD/nm 18.6 (8.7 – 30.6 nm, PdI = 0.156, N = 3).

TEM (100 kV, "holey" carbon film): APD/nm 16.3 ± 1.5 (10.9 – 20.2 nm, N = 100).

Modification and characterisation of multi-walled carbon nanotubes (MWNT)

Multi-walled carbon nanotubes (60.4 mg, Nanocyl #3100) were ground using a pestle and mortar for 15 min to yield a black solid (60.4 mg, 100 % wt.).

IR (KBr): υ/cm^{-1} 1637s, 1383m.

UV-vis (H$_2$O): λ/nm 254.65 (54.38 mL mg^{-1} cm^{-1}).

TEM (100 kV, "holey" carbon film): ATL/μm 2.04 ± 0.32 (0.6 – 4.6 μm, N = 20); ATD/nm 9.2 ± 2.2 (5.5 – 13.9 nm, N = 50).

Assembly of gold nanoparticle – carbon nanotube composite materials

For each experiment, a known mass of nanotubes (0.01 mg for variation of pH; 0.05 mg for variation of ionic strength) was added to a known volume of gold nanoparticles (3 mL, concentration = 4.90x10^{12} NP mL^{-1} for variation of pH, 5.37x10^{12} NP mL^{-1} for variation of ionic strength) . The heterogeneous mixture was sonicated for 30 mins at room temperature, the suspension filtered through a 0.2 μm cellulose acetate syringe filter and the supernatant characterised by UV-vis spectroscopy.
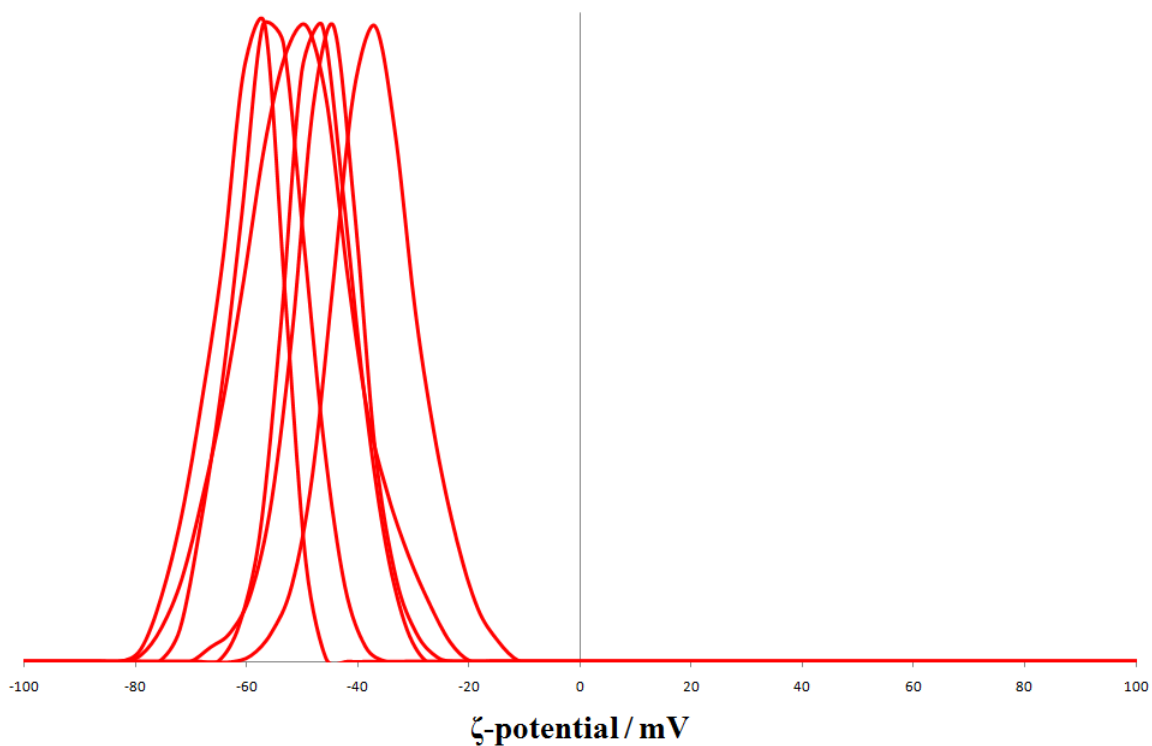
### S.2. *Characterisation of surface charge by ζ-potential analyses*
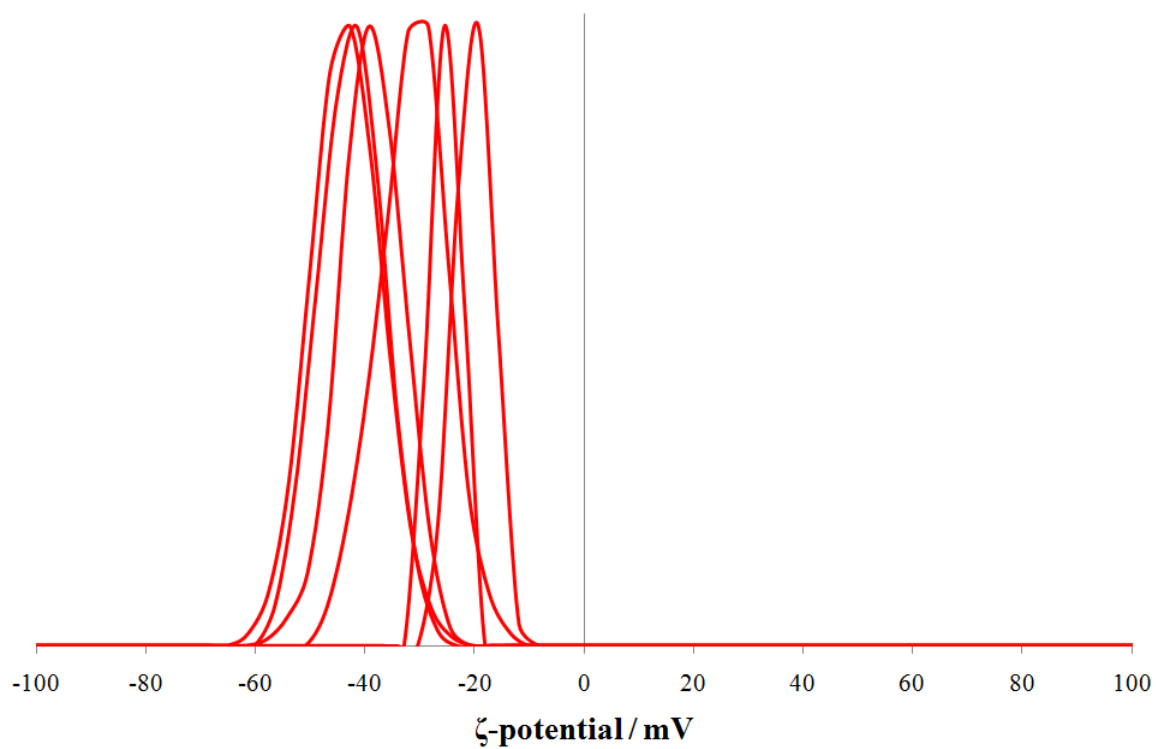
Figure S.1. ζ-potential analysis of AuNP as a function of pH (pH = 2.9, 3.8, 5.1, 6.1, 7.1 and 7.6, right to left).
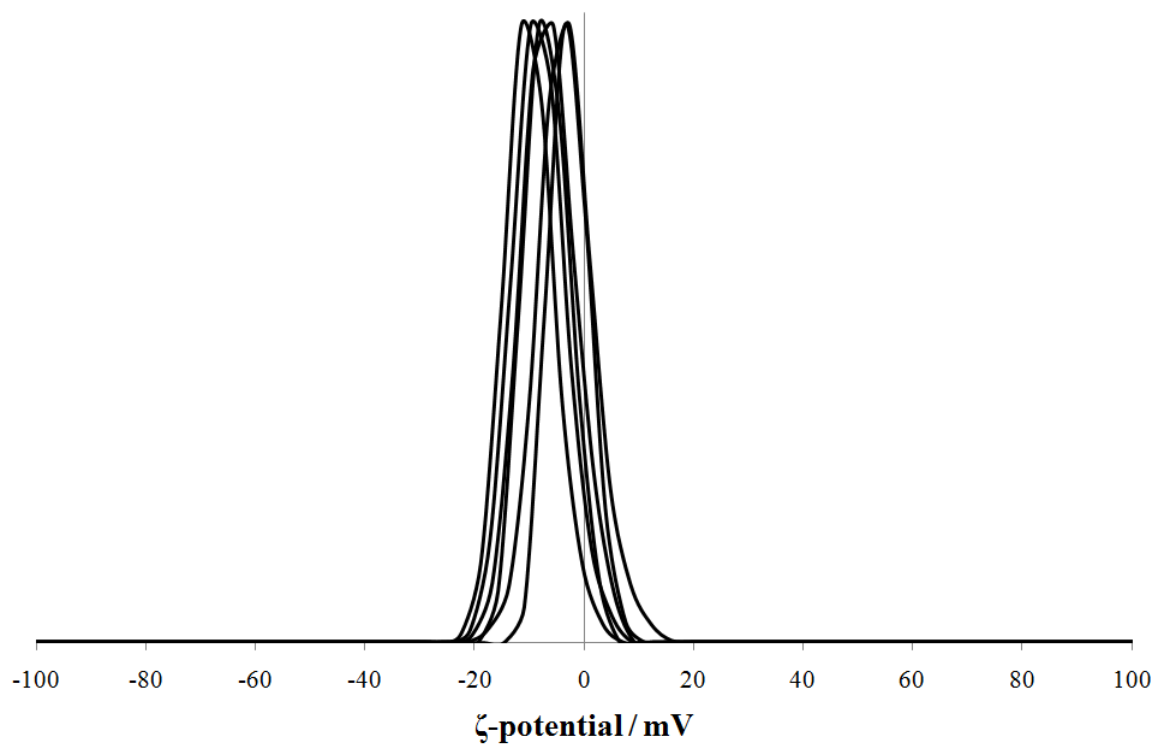
Figure S.2. ζ-potential analysis of MWNT as a function of pH (pH = 2.9, 3.8, 5.1, 6.1, 7.1 and 7.6, right to left).

Figure S.3. ζ-potential analysis of AuNP as a function of ionic strength (I = 0.0006, 0.003, 0.006, 0.015, 0.03 and 0.06 mol dm^{-3}, left to right).
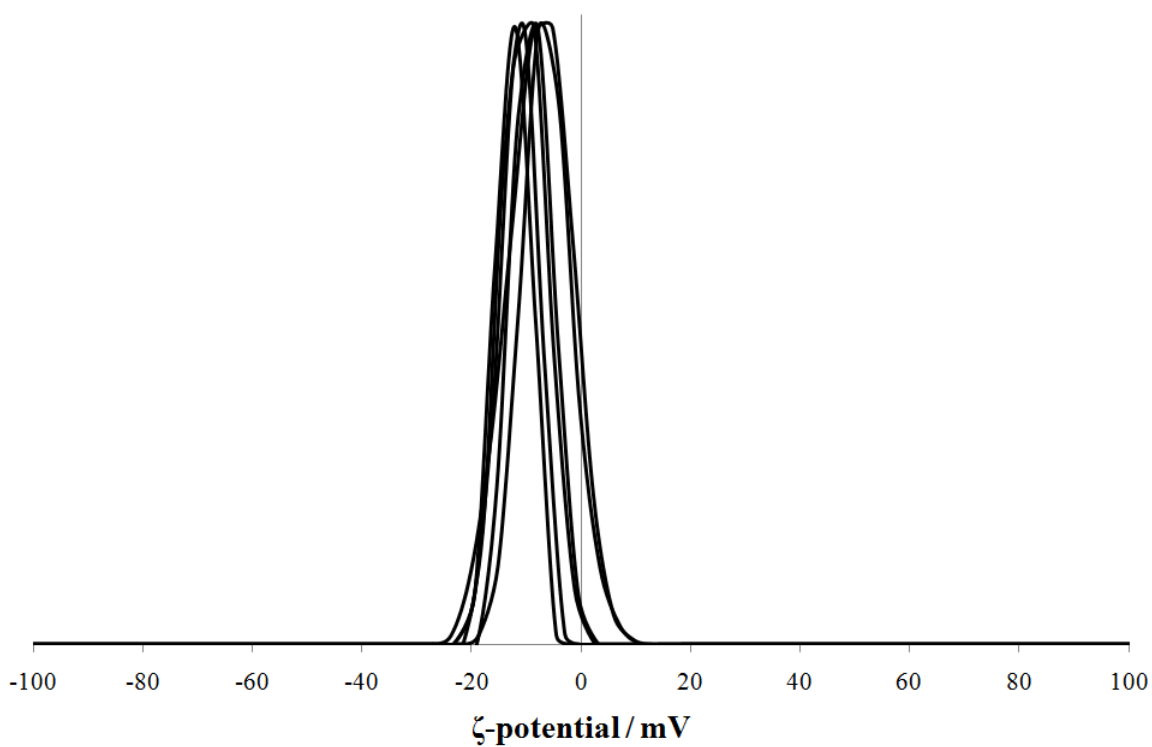
Figure S.4. ζ-potential analysis of MWNT as a function of ionic strength (I = 0.0006, 0.003, 0.006, 0.015, 0.03 and 0.06 mol dm^{-3}, left to right).

S.3. *Calculation of the magnitude of electrostatic forces*

Conversion of the recorded ζ-potential into the magnitude of electrostatic forces was determined using a combination of the theories established by Fitzmaurice *et al.*[28,29] and Ohshima *et al.*[30,31] ζ-potential (in mV) was initially converted into surface charge density (in C m^{-2}) using the equations for distribution of charge around a sphere (AuNP) and a cylinder (MWNT)[30] of known dimensions respectively. Surface charge density was next converted into total charge per active surface area (in C)[30,31] – the active surface area of the components were determined by approximating ellipses overlaid on the surface of a sphere (AuNP) and a cylinder (MWNT) respectively. Relative magnitude of electrostatic force (in N) was calculated using Coulomb's inverse square law – the distance between charges was assumed to be 3 nm as this is the distance where all short-range, attractive interactions tend to zero[29] and as such this is the position of maximum electrostatic repulsion.