Interactions of carbon nanotubes and gold nanoparticles: the effects of solvent dielectric constant and temperature on controlled assembly of superstructures

G. A. Rance\textsuperscript{a}\textsuperscript{*} and A. N. Khlobystov\textsuperscript{a,b}

\textsuperscript{a} School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, U.K.

\textsuperscript{b} Nottingham Nanotechnology and Nanoscience Centre, University of Nottingham, University Park, Nottingham, NG7 2RD, U.K.

E-mail: Graham.Rance@nottingham.ac.uk

S1. The effect of surface charge on nanoparticle-nanotube interactions

S1.1. General experimental

Infra-red (IR) spectra were measured as KBr discs using a Nicolet 380 FT-IR spectrometer over the range 4000-400 cm\textsuperscript{-1}. Dynamic light scattering (DLS) and phase analysis light scattering (PALS) were performed using a Malvern Instruments Nano-ZS Zetasizer at room temperature. Samples were pre-treated by syringe filtration (cellulose acetate, 0.45 \( \mu \)m) to remove dust and other large non-nanoparticle impurities prior to measurement. Average particle diameters (\( d_{NP^*} \)) are quoted in units of nm. Polydispersity index (PdI) is dimensionless. Values of \( \zeta \) potential were recorded from solutions of comparable pH and ionic strength. Quoted values are the average of three measurements.

S1.2. Synthesis of AuNP\textsuperscript{+}

To tetrachloroauric acid trihydrate (125 mg, 0.32 mmol, 1 eq.) was added deionised water (10 mL) and the mixture stirred for 10 min yielding a bright yellow solution. A separate solution containing tetaoctylammonium bromide (765 mg, 1.40 mmol, 4.4 eq.) in toluene (25 mL) was also stirred for 10 min and then added with vigorous stirring to the aqueous gold solution, resulting in a biphasic mixture, consisting of an upper orange organic layer and a lower colourless aqueous layer. A further solution of sodium borohydride (131 mg, 3.46 mmol, 10.8 eq.) in deionised water (8 mL) was stirred for 10 min and then added to the biphasic mixture, resulting in an instant colour change in the organic layer from orange to ruby red / purple. This was then vigorously stirred for 48 hr at room temperature. The biphasic mixture was then separated, retaining the organic layer which was washed with water (3 x 20 mL) and dried over anhydrous sodium sulphate. The organic layer was next diluted with toluene (35 mL) and added to an aqueous solution of 4-dimethylaminopyridine (DMAP, 730 mg, 5.98 mmol, 18.7 eq.) in deionised water (60 mL) and left for 20 hr at room temperature with no further agitation. The resultant biphasic mixture, consisting of an upper colourless organic layer and a lower ruby red aqueous layer, was separated, retaining the aqueous phase to yield a ruby red solution of 4-(dimethylamino)pyridine-stabilised gold nanoparticles (AuNP@DMAP, hereafter referred to as AuNP\textsuperscript{+}). \( ^{1} \)H NMR (300 MHz, D\textsubscript{2}O): \textit{\textdelta}/ppm 8.20 (d, 2H, \( J = 6.6 \) Hz), 6.48 (d, 2H, \( J = 6.6 \) Hz), 2.99 (s, 6H). UV-vis (H\textsubscript{2}O): \( \lambda /nm \) 521.4 (\( c = 2.6x10^7 \)). DLS (H\textsubscript{2}O): \( d_{NP^*}/nm \) 9.4 (5.6 – 32.1 nm, PdI = 0.29). PALS (H\textsubscript{2}O): \( \zeta /mV \) +18.2 ± 5.6. TEM (100 kV, continuous carbon film): \( d_{NP^*}/nm \) 6.4 ± 0.6 (4.7 – 7.8 nm).
S1.3. Synthesis of AuNP

To an aqueous solution of AuNP@DMAP (40 mL) was added a separate solution of 11-mercaptoundecanoic acid (MUA, 60 mL, 0.45M in ethanol, adjusted to pH10 with 10 % wt. potassium hydroxide in deionised water) and the resulting mixture left to stand overnight. The resulting colourless solution containing a purple precipitate was subject to brief sonication, followed by purification by centrifugation (8,000xg, 30 min). The colourless supernatant was decanted and discarded, the purple precipitate dissolved in the minimum volume of 10%wt. potassium hydroxide and purified by flash chromatography on Sephadex LH-20 (10%wt. potassium hydroxide) to yield a ruby red solution of 11-mercaptoundecanoate-stabilised gold nanoparticles (AuNP@MUA, hereafter referred to AuNP). UV-vis (H₂O): λ/nm 519.9 (ε = 2.6x10⁷). DLS (H₂O): d₅₃*/nm 9.4 (5.2 – 31.8 nm, PdI = 0.29). PALS (H₂O): ζ/mV –29.2 ± 5.3. TEM (100 kV, continuous carbon film): d/NP/nm 6.4 ± 0.7 (4.7 – 8.0 nm).

S1.4. Pre-treatment of MWNT

Multi-walled carbon nanotubes (60.4 mg, Nanocyl #3100 MWNT, CVD) were ground using a pestle and mortar for 15 min to yield a black solid (60.4 mg, 100%wt.). IR (KBr): ν/cm⁻¹ 1637s (νC=), 1383m (νC=C). UV-vis (H₂O): λ/nm 269.9 (ε* = 54.4). PALS (H₂O): ζ/mV –11.4 ± 5.9. TEM (100 kV, “holey” carbon film): lNT/μm 2.0 ± 0.4 (0.2 – 2.5 μm); idNT/nm 4.4 ± 1.6 (2.5 – 8.7 nm); odNT/nm 9.2 ± 2.2 (5.5 – 13.9 nm); WNT 10 ± 2.

S1.5. Assembly of AuNP/MWNT superstructures

In each experiment, a known mass of nanotubes (0 – 0.5 mg) was added to a known volume of nanoparticles in aqueous suspension (3 mL, concentration = 1.4x10¹³ NP mL⁻¹). The heterogeneous mixture was bath sonicated (Langford Sonomatic 375) for 30 min at room temperature (22 °C), allowed to settle for 30 min at room temperature, the supernatant characterised by UV-vis spectroscopy and the solid precipitate by transmission electron microscopy.
**Figure S1.** UV-vis spectroscopic analysis of (a) AuNP⁺ and (b) AuNP⁻ supernatants subsequent to mixing with MWNT. The surface area of MWNT was varied between (a) $0 – 1.50 \times 10^{27}$ nm$^2$ and (b) $0 – 1.35 \times 10^{28}$ nm$^2$, top to bottom. (c) PALS analysis of positive (blue, $\zeta = +18.2 \pm 5.6$ mV) and negative (red, $\zeta = -29.2 \pm 5.3$ mV) AuNP and MWNT (black, $\zeta = -11.4 \pm 5.9$ mV). Spectra have been normalised for clarity. (d) Adsorption isotherm correlating the number ($n_{NP}$) of positive (blue line, $n_{NP} = 1 \times 10^{-41}(SA_{NT})^2 + 6 \times 10^{-15}(SA_{NT})$, correlation factor = 0.9969) and negative AuNP (red line, $n_{NP} = 2 \times 10^{-41}(SA_{NT})^2 + 2 \times 10^{-16}(SA_{NT})$, correlation factor = 0.9988) independently adsorbed onto MWNT with carbon nanotube surface area ($SA_{NT}$, in nm$^2$). The horizontal dotted line refers to the total number of nanoparticles in starting solution ($4.2 \times 10^{13}$). Bars reflect the mean standard deviation from repeat measurements. TEM imaging of (e) AuNP⁺-MWNT and (f) AuNP⁻-MWNT hybrid materials. The white arrows guide the eye to the precise location of some adsorbed nanoparticles. Scale bars are 100 nm.

<table>
<thead>
<tr>
<th>Nanoparticle</th>
<th>$\theta_NP$ / NP μm$^{-1}$</th>
<th>$\theta_NP'$ / NP nm$^{-2}$</th>
<th>$S_{NP}$ / nm</th>
<th>$n_{NP}$</th>
</tr>
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<tbody>
<tr>
<td>AuNP⁺</td>
<td>20.2 ± 2.0</td>
<td>7.0x10$^{-4}$</td>
<td>50</td>
<td>3.2x10$^{13}$</td>
</tr>
<tr>
<td>AuNP⁻</td>
<td>0.5 ± 0.4</td>
<td>1.7x10$^{-5}$</td>
<td>2000</td>
<td>7.5x10$^{11}$</td>
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</tbody>
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Scheme S2. Schematic representation of the mechanism of nanoparticle adsorption on nanotubes: (a) in systems of opposite charge and (b) in systems of like charge. The colour and size of the arrows relate to the type (red is repulsive, blue is attractive) and magnitude of interactions respectively. Surface functional groups have been omitted for simplicity. Surface charges have been simplified for clarity. The energy profiles illustrate relative changes in the barrier to adsorption subsequent to binding of the first nanoparticle (full line is prior to adsorption, dashed line is subsequent to adsorption). Assuming the system to be dynamic and that the kinetic energy of nanoparticles ($E_{kin}$) is of sufficient magnitude, collisions between nanoparticles and nanotubes are probable. The ultimate fate of the majority of these collisions depends on the specific kinetic energy of the incoming nanoparticle so that only a small proportion of collision events will result in adsorption on nanotubes. In systems of opposite charge, the affinity towards adsorption is completely dominated by attractive electrostatic forces ($E_{elec}$), which are both strong and long-range. Subsequent adsorption of additional nanoparticles is subtly hindered by a slight decrease in the attractive electrostatic interactions ($E_{elec'}$), a consequence of the summated net charge of nanotubes (n⁻) and the first adsorbed nanoparticle (m⁺). The resultant charge of the composite material diminishes with further adsorption of nanoparticles until a state of charge neutrality (or slight residual positive charge) is achieved and the process halts. In this way, adsorption of nanoparticles on nanotubes can be considered self-terminating. In systems of like charge, however, the adsorption is dependent on nanoparticles initially overcoming the barrier provided by repulsive electrostatic forces and adsorbing due to attractive interactions, associated with van der Waals forces ($E_{vdW}$) and possibly charge transfer and hydrophobic interactions, which are comparably weaker and shorter range. Successive adsorption of additional nanoparticles is deterred by an increase in repulsive electrostatic interactions ($E_{elec'}$). Thus, nanoparticles with higher kinetic energy ($E_{kin'}$) are required for successful collisions to occur. This accumulation of charge in composites continues with the further adsorption of nanoparticles until incoming nanoparticles are unable to overcome the repulsive barrier and the process self-terminates.
S2. The effect of solvent dielectric constant and temperature on nanoparticle-nanotube interactions

S2.1. General experimental

$^1$H NMR spectra were obtained using either a Bruker DPX300 (300.13 MHz) spectrometer at 300 K. IR spectra were measured using a Nicolet 380 FT-IR spectrometer over the range 4000-400 cm$^{-1}$. Microanalysis was performed by the University of Nottingham, School of Chemistry Microanalytical Service on a Perkin-Elmer 240B instrument.

S2.2. Synthesis and characterisation of AuNP

The method outlined in the pioneering studies of Brust et al.$^{20}$ was employed for the preparation of gold nanoparticles. An aqueous solution of tetrachloroauric acid trihydrate (7.9 mL of a 1% wt. stock solution, 0.2 mmol, 1 eq.) was added to deionised water (22.1 mL) and stirred for 10 min yielding a bright yellow solution. A separate solution containing tetraoctylammonium bromide (0.219 g, 0.4 mmol, 2 eq.) in toluene (60 mL) was also stirred for 10 min and then added with vigorous stirring to the aqueous gold solution, resulting in a biphasic mixture, consisting of an upper orange organic layer and a lower colourless aqueous layer. A separate solution of dodecanethiol (0.016 mL, 0.07 mmol, 0.3 eq.) in toluene (10 mL) was stirred for 10 min and then added to the biphasic mixture, resulting in a gradual colour change in the organic layer from orange to milky yellow. A further solution of sodium borohydride (0.076 g, 2 mmol, 10 eq.) in deionised water (30 mL) was stirred for 10 min and then added to the biphasic mixture, resulting in an instant colour change in the organic layer from milky yellow to brown/black. This was then vigorously stirred for 20 hr at room temperature. The biphasic mixture was then separated, retaining the organic layer which was washed with water (2 x 200 mL) and dried over anhydrous sodium sulphate. The solvent was removed in vacuo, the resultant dark brown liquid added to ethanol (350 mL) and cooled to $-30^\circ$C for 12 hr. The brown precipitate was collected by vacuum filtration (0.2 µm polytetrafluoroethylene (PTFE) membrane), washed with ethanol (100 mL) and acetone (100 mL) and sucked dry to yield a brown solid (25.3 mg). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$/ppm 1.30 (s br, 20H), 0.92 (s br, 3H). IR (neat): $\nu$/cm$^{-1}$ 2955w ($\nu$C-H), 2919s ($\nu$C-H), 2872w ($\nu$C-H), 2850m ($\nu$C-H). UV-vis (C$_6$H$_5$CH$_3$) $\lambda$/nm 515.1 ($\epsilon$ = 1.3x10$^6$, $\epsilon^*$ = 8.8). Microanalysis found: C, 19.81; H, 3.33 %. TEM (200 kV): $d_{NP}$/nm 2.8 ± 0.5 (1.3 – 4.2 nm).
S2.3. **TEM characterisation of the AuNP/MWNT hybrid materials**

**Figure S2.** TEM analysis of the AuNP/MWNT assembled in toluene.
S2.4. Adsorption kinetics

Figure S3. Application of the Arrhenius relationship to determine the apparent activation barrier for AuNP adsorption on MWNT, $E_a = 9.6$ kJ mol$^{-1}$ and $A = 1.3 \times 10^{-8}$. As [MWNT] in solution is immeasurably low due to inherent issues of solubility (below the limit detectable by spectroscopic means), we can assume that [MWNT] in organic solution is negligible. Therefore, we can apply the isolation method and approximate a pseudofirst-order rate law for adsorption of AuNP and MWNT depending only on [AuNP], consistent with previous studies probing the adsorption of aromatic dye molecules onto carbon nanotubes.$^{37-39}$
S2.5. Reversibility of AuNP-MWNT interactions

To evaluate the reversibility of AuNP-MWNT interactions, the AuNP/MWNT composite assembled at 60 °C was isolated by vacuum filtration (0.2 μm PTFE), washed with toluene (10 mL, in 5 x 2 mL portions) to ensure that all non-adsorbed nanoparticles were removed. It is important to note that the colour of the filtrate was colourless after the final portions of toluene were added. The black solid was briefly dried and then added to toluene (3 mL) and the suspension stirred at 60 °C for 24 hr. The solid was obtained from vacuum filtration (0.2 μm PTFE) and the number of nanoparticles desorbed from the composite obtained by UV-vis spectroscopy analysis of the filtrate.

![Figure S4](image)

**Figure S4.** UV-vis spectroscopic analysis of (i) the initial solution of AuNP (NP\textsubscript{init}, top), (ii) the solution of AuNP subsequent to assembly with MWNT at 60°C after 24 hr (NP\textsubscript{ads}, middle) and (iii) the solution of AuNP subsequent to desorption from AuNP/MWNT at 60°C after 24 hr (NP\textsubscript{des}, bottom). These measurements indicate that 1.81x10\textsuperscript{15} NP are adsorbed onto MWNT from bulk suspension following homogenisation at elevated temperature. After addition of fresh solvent and subsequent homogenisation, a total of 3.27x10\textsuperscript{14} NP desorb from the surface of the AuNP/MWNT superstructure. This represents 18% of the initially adsorbed nanoparticles and clearly shows that the interactions between AuNP and MWNT are reversible.