

Supporting Information for:

One-Pot Nucleation, Growth, Morphogenesis, and Passivation of 1.4 nm Au Nanoparticles on Self-Assembled Rosette Nanotubes

Rahul Chhabra,^{†‡} Jesus G. Moralez,^{†‡} Jose Raez,^{†‡} Takeshi Yamazaki,^{†¶}
Jae-Young Cho,[†] Andrew J. Myles,[†] Andriy Kovalenko^{†¶} and Hicham Fenniri^{†‡*}

[†]National Institute for Nanotechnology (NINT-NRC), [‡]Department of Chemistry, [¶]Department of Mechanical Engineering, University of Alberta, 11421 Saskatchewan Drive, Edmonton, Alberta T6G 2M9, Canada

Experimental Section

AFM measurements. Samples were prepared by placing 5 μ L of the RNTs on freshly cleaved mica surface and left to adsorb for 2 minutes. The excess sample was wicked by clean piece of filter paper. Nanotubes were then imaged using a Digital Instruments/Veeco Instruments MultiMode Nanoscope IV AFM equipped with an E scanner. Silicon cantilevers (MikroMasch USA, Inc.) with low spring constants of 4.5 N/m were used in tapping mode (TM-AFM). To obtain a clear image with high resolution low scan rate (0.5-1 Hz) and amplitude set point (1 V) were chosen during measurement.

Electron microscopy. The samples were deposited on carbon-coated 400-mesh copper grids and left to adsorb for 20 seconds. The grid was then blotted with a clean piece of filter paper and dried in vacuum for 30 minutes at 110°C. The samples were imaged by scanning electron microscopy (SEM) using a Hitachi S-4800 (with a field-emission gun) working at 10 kV. TEM images were obtained with JEOL 2200 FS TEM Schottky field emission instrument equipped with an in-column omega filter working at 200 kV. The electron diffraction data were collected using a JEOL 3000F transmission electron microscope working at 300 kV, equipped with a post column energy filter. The electron diffraction patterns were collected using a 1024 x 1024 pixel slow scan camera with 14 bit dynamic range, mounted directly below the viewing screen of the microscope.

Modeling. The most stable conformation of the RNTs made of twin G \wedge C module was obtained by using Macromodel 8.5 and 3D-RISM theory as reported earlier.¹ Starting with this structure, the side-chain conformation was modified by using Macromodel 8.5 so that the large AuNP can fit the "nest" consists of four side chains. The molecular figures were generated by VMD.²

References

1. Moralez, J. G.; Raez, J.; Yamazaki, T.; Motkuri, R. K.; Kovalenko, A.; Fenniri, H. *J. Am. Chem. Soc.* **2005**, *127*, 8307-8309.
2. Humphrey, W.; Dalke, A.; Schulten, K. *J. Mol. Graph.* **1996**, *14*, 33-38.

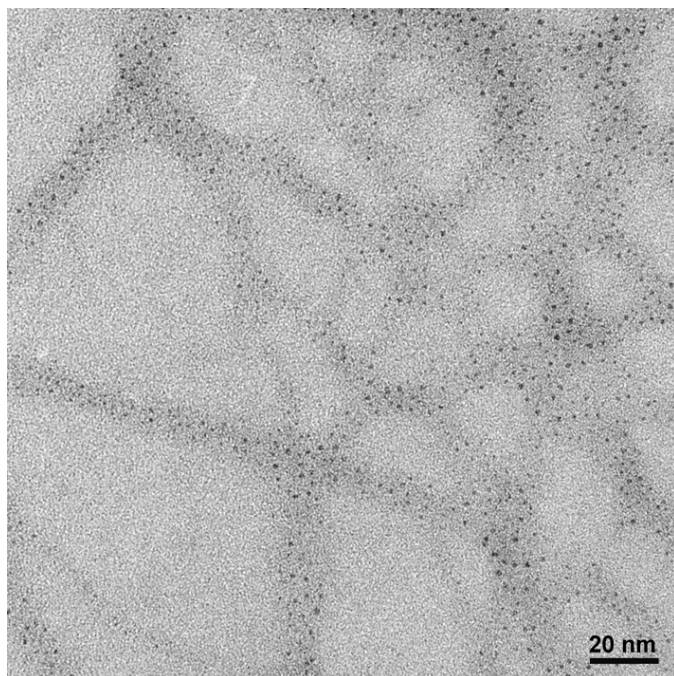


Figure S1. Representative TEM image of RNTs (50 μ M) with Au NPs.

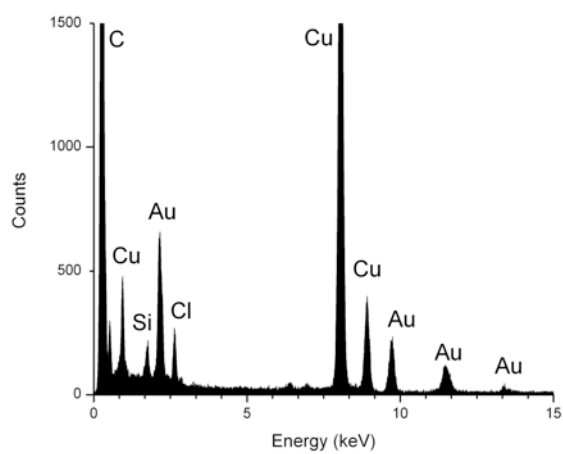


Figure S2. EDX spectrum of Au NPs templated by RTNs.

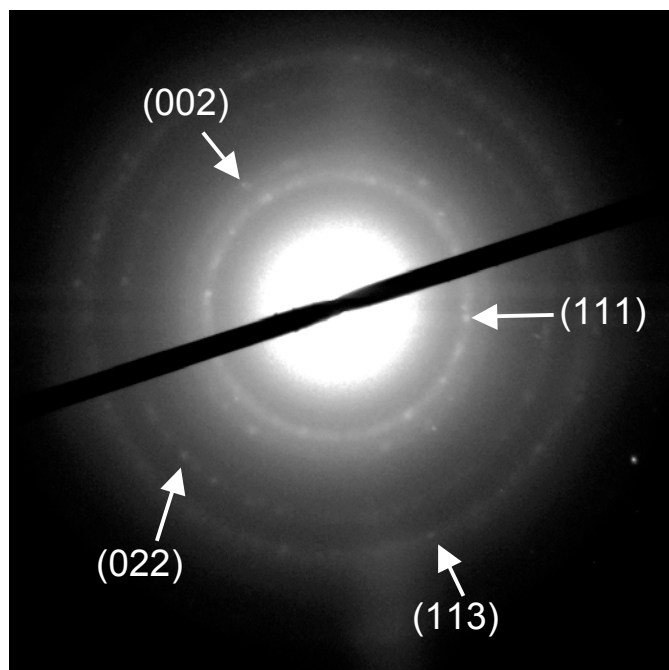


Figure S3. Selected area electron diffraction of RNTs covered with AuNPs showing the (111), (002), (022) and (133) reflections of metallic gold.

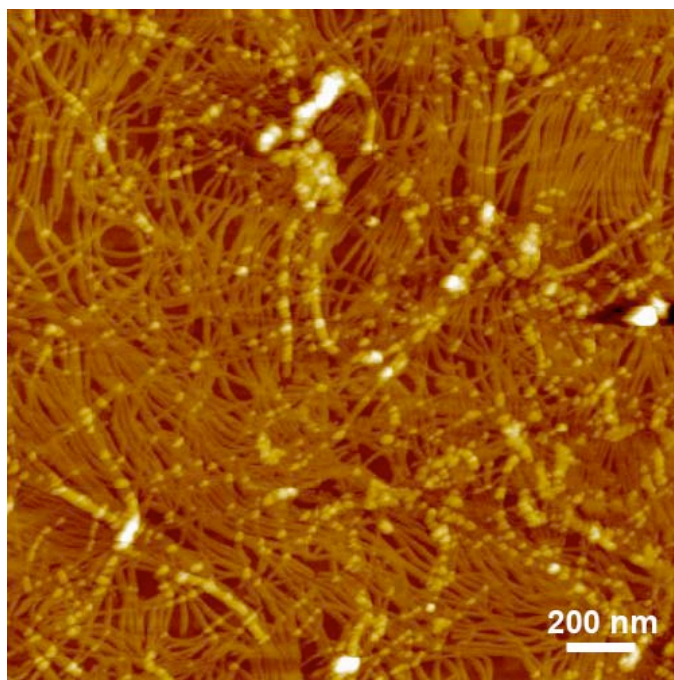
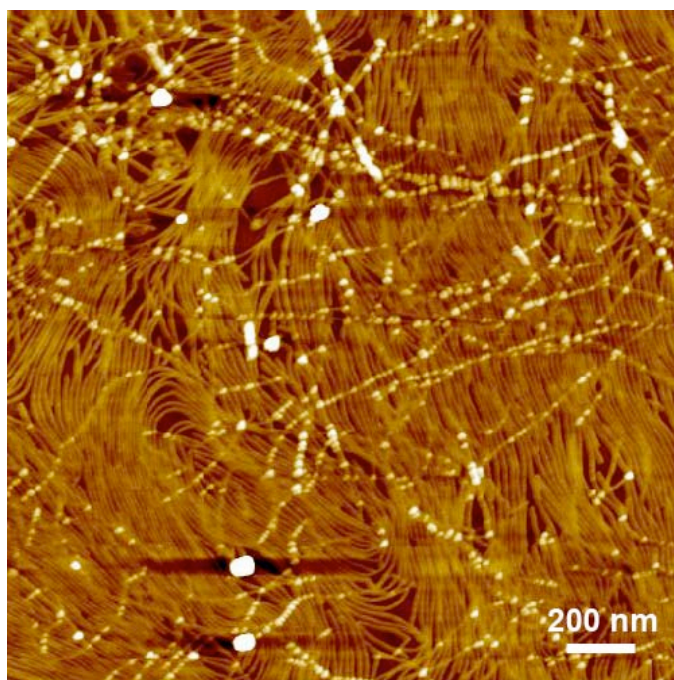


Figure S4. Additional AFM images of the self-assembled RNTs.

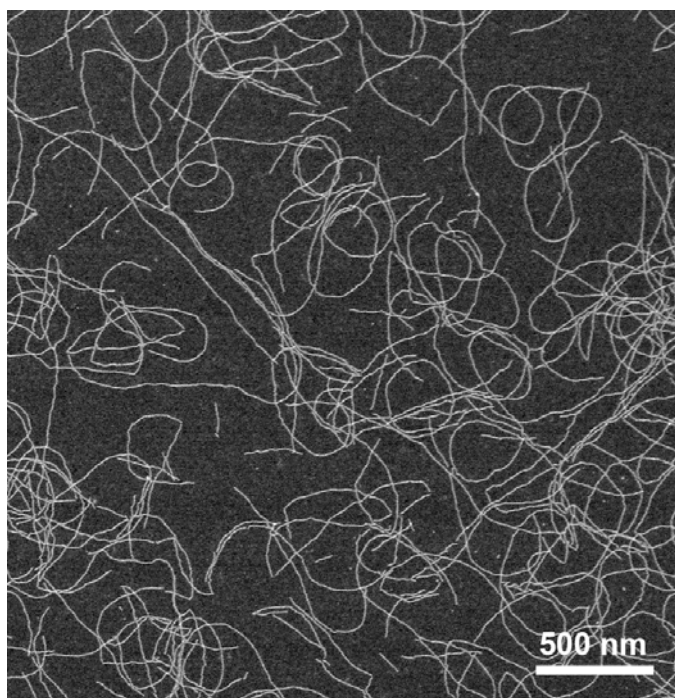
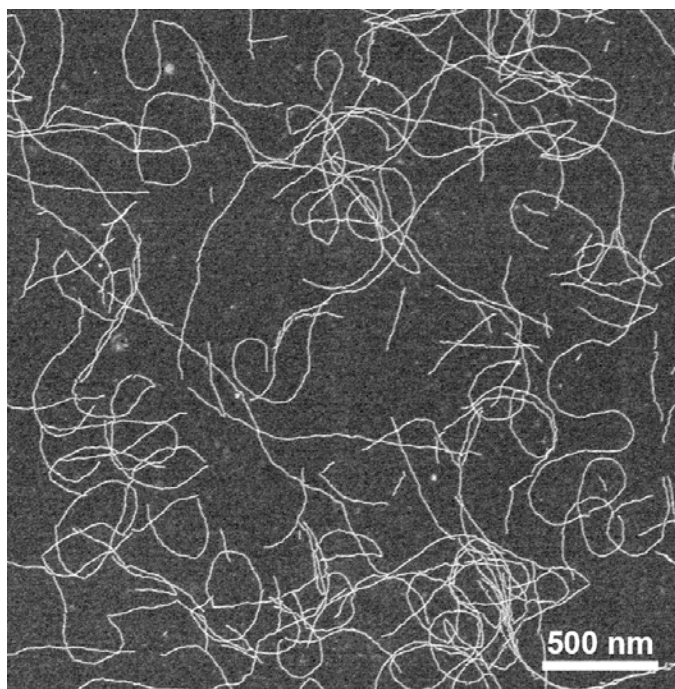


Figure S5. Additional SEM images of the self-assembled RNTs.

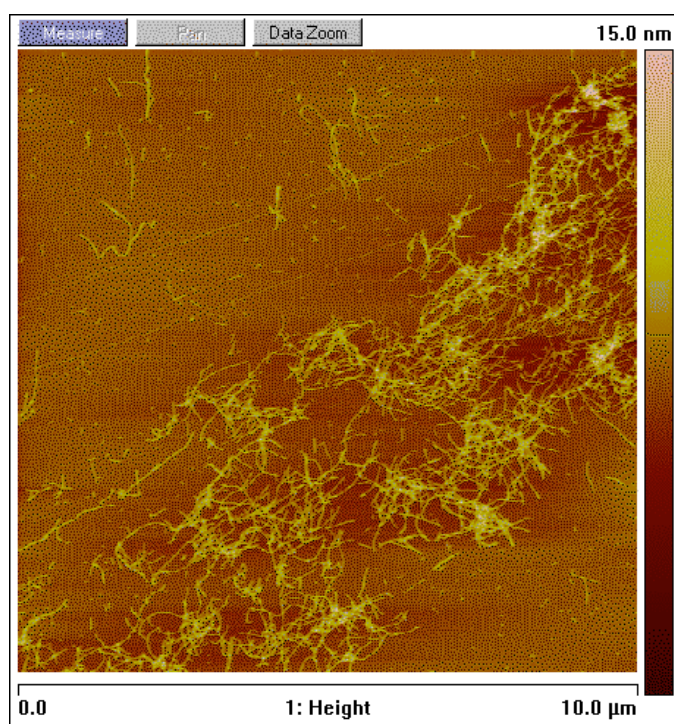
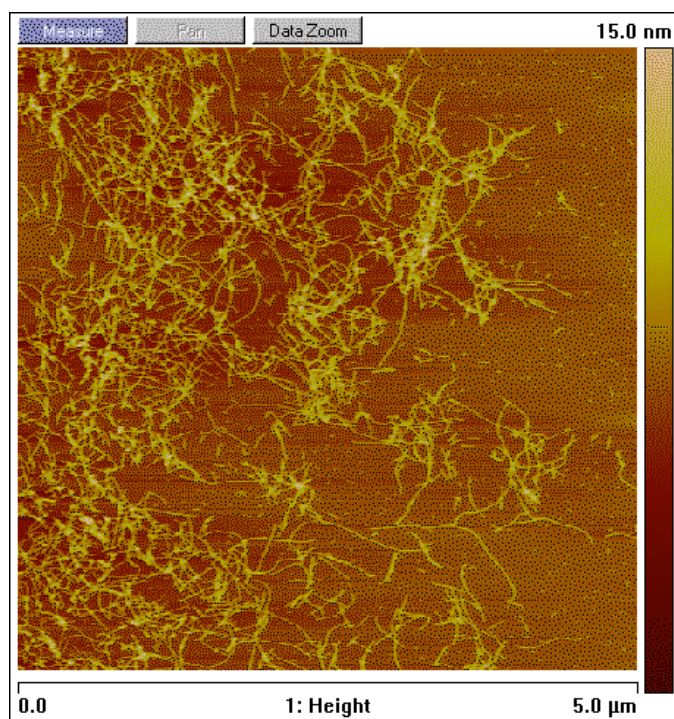


Figure S6. Additional AFM images of the RNTs (1 mM) with Au NPs.

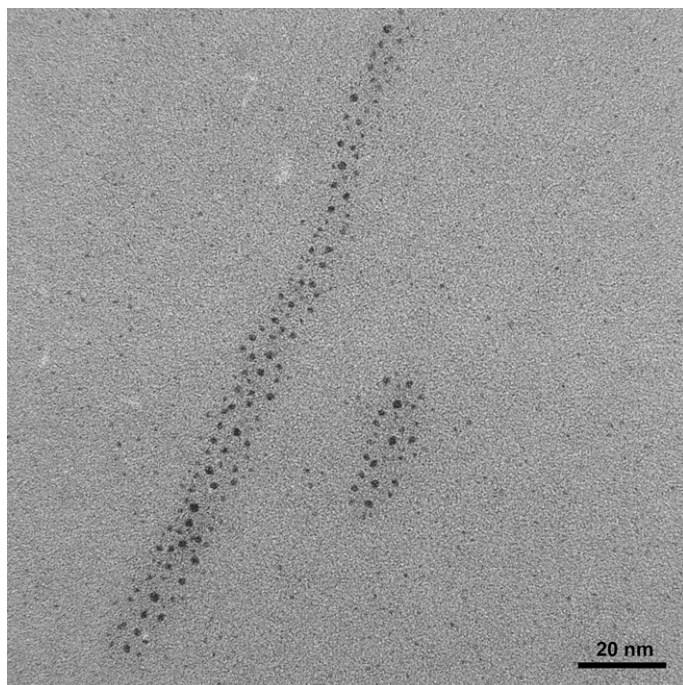


Figure S7. Additional TEM images of the RNTs (1 mM) with Au NPs.

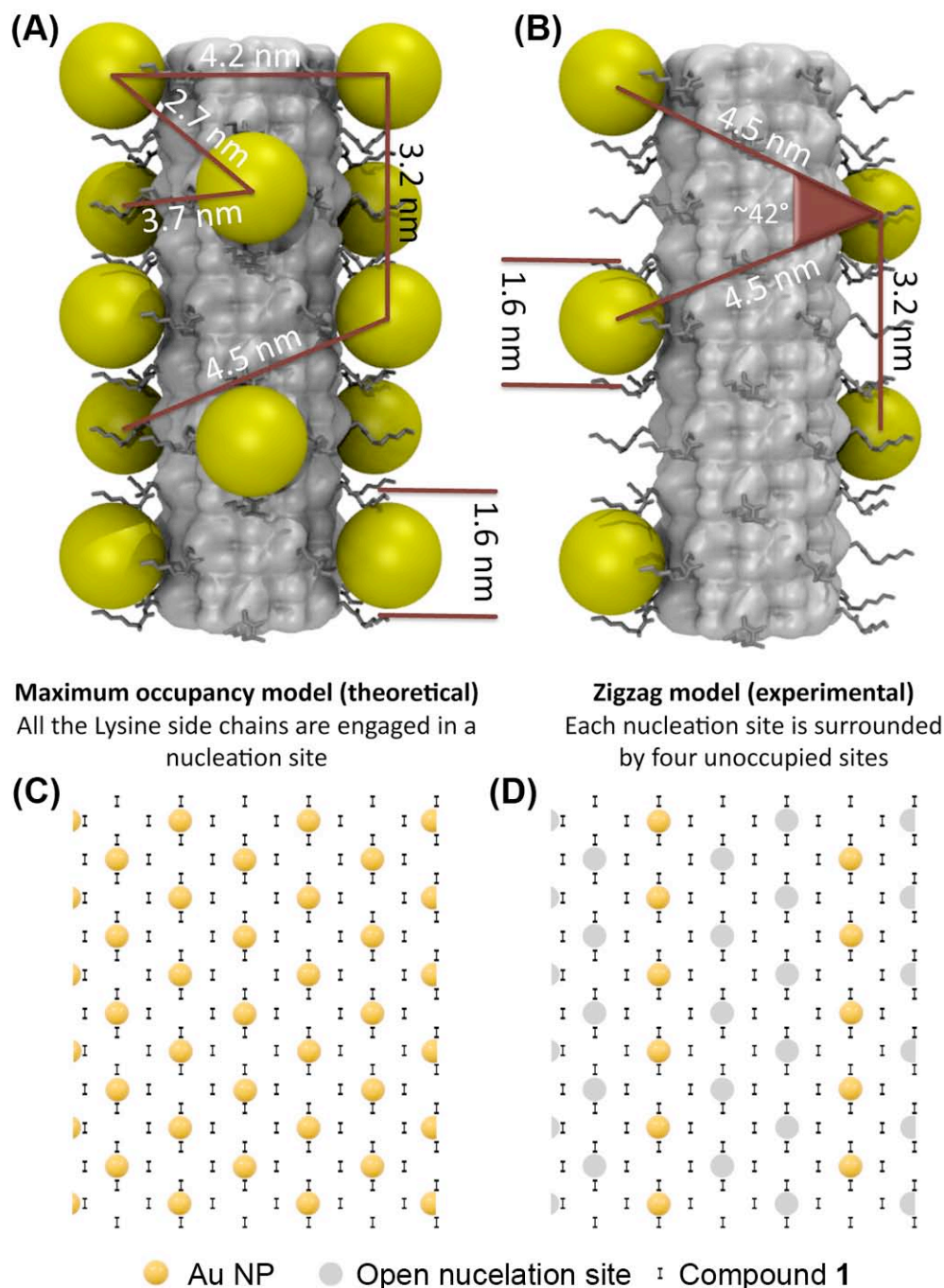


Figure S8. Maximum occupancy model (A, C) and Zigzag model (B, D). A statistical analysis revealed that out of the maximum number of sites (188 sites/100 nm) only $\sim 30\%$ are filled (58 sites/100 nm). This figure shows two models, a theoretical maximum occupancy model (A, C) and a zigzag model based on TEM measurements (B, D). The zigzag model not only accounts for the $\sim 30\%$ loading and interparticle distances measured, but it also reduces interparticle repulsion as each nucleation site is surrounded with four open sites (grey circles in D).

The Au NPs appeared almost exclusively on the RNTs thus suggesting that coordination of the AuCl_4^- to the ammonium sites on the RNTs probably reduces their redox potential. These experiments have also established that RNTs tend to bundle massively after treatment with AuCl_4^- ions, most likely the result of the formation of stable RNT/ AuCl_4^- coordination complexes leading to charge neutralization, and subsequent bundling. Attempts to control this behavior by decreasing the concentration of compound **1**, sonication, use of co-solvents in various ratios, use of surfactants were unsuccessful (Figure S9). Our next step is to try to extract the NPs into an organic phase (e.g. toluene solution of mercaptanes), which may not only offset the bundling problem but would also allow the use of the RNTs in catalytic amount.

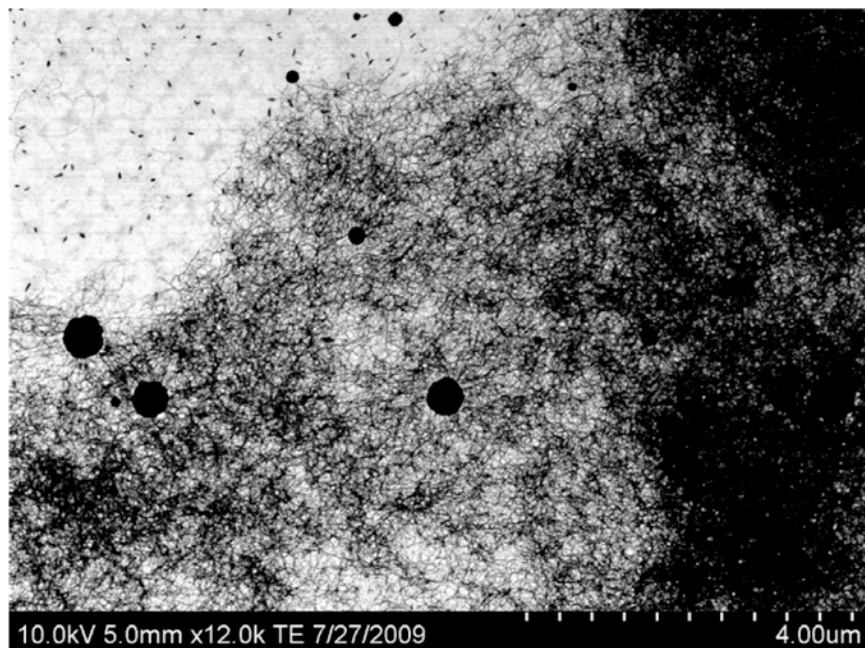


Figure S9A. STEM image of RNTs (50 μM) incubated with HAuCl_4 (20 equivalents).

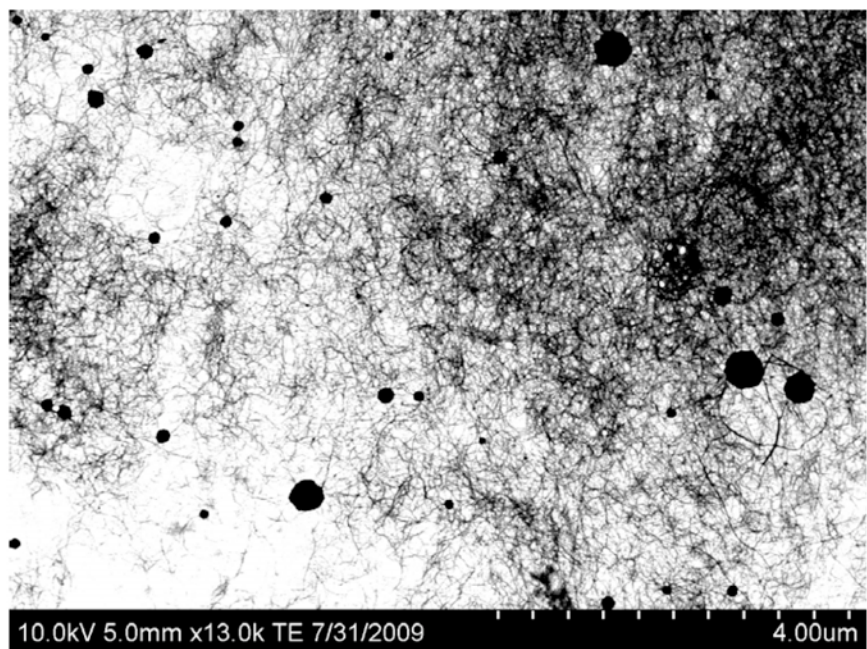


Figure S9B. STEM image of RNTs (10 μ M) incubated with HAuCl_4 (20 equivalents).

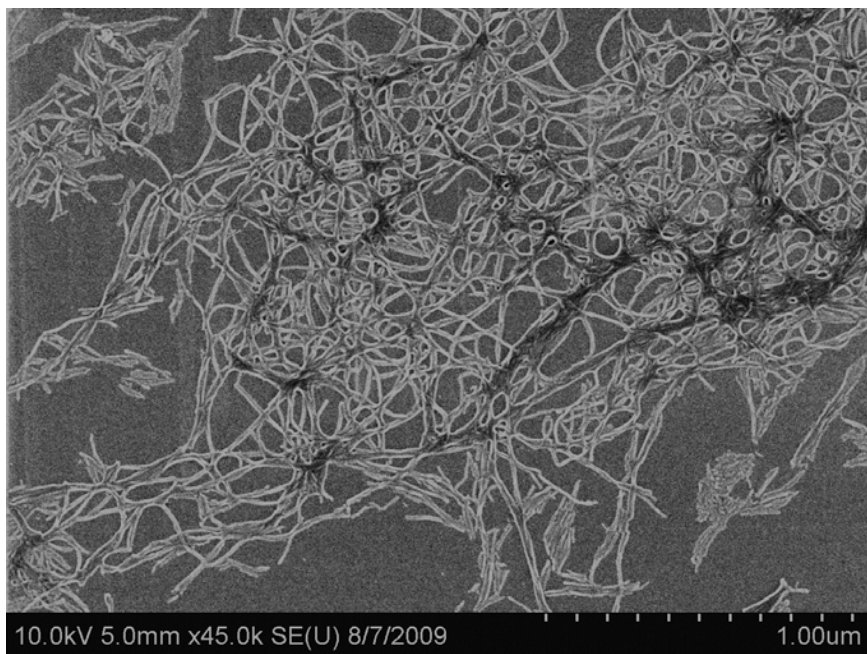


Figure S9C. SEM image of RNTs (50 μ M) incubated with HAuCl_4 (20 equivalents) and sonicated overnight.

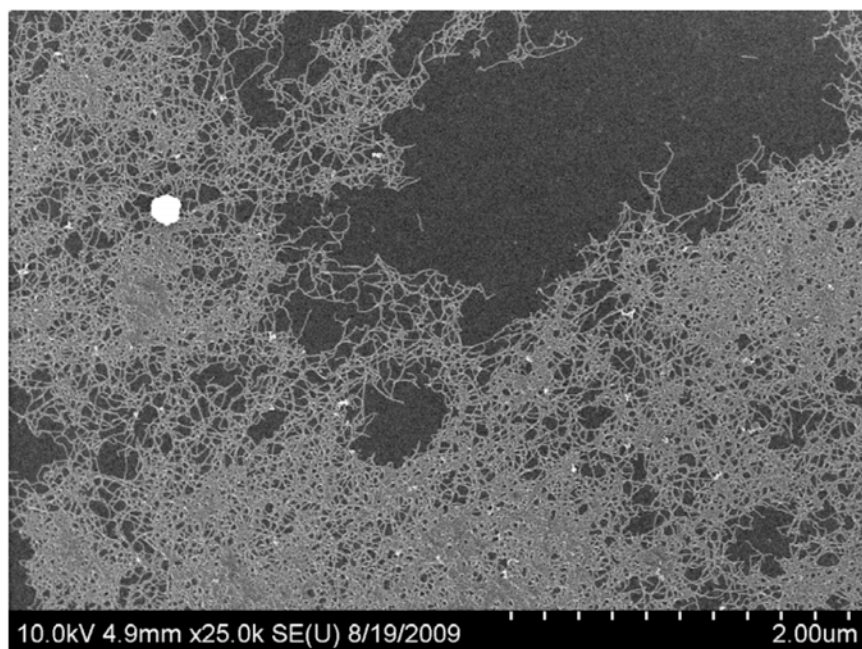


Figure S9D. SEM image of RNTs (50 μM) incubated with H_2AuCl_4 (20 equivalents) $\text{H}_2\text{O}:\text{CH}_3\text{OH}$ (75:25).

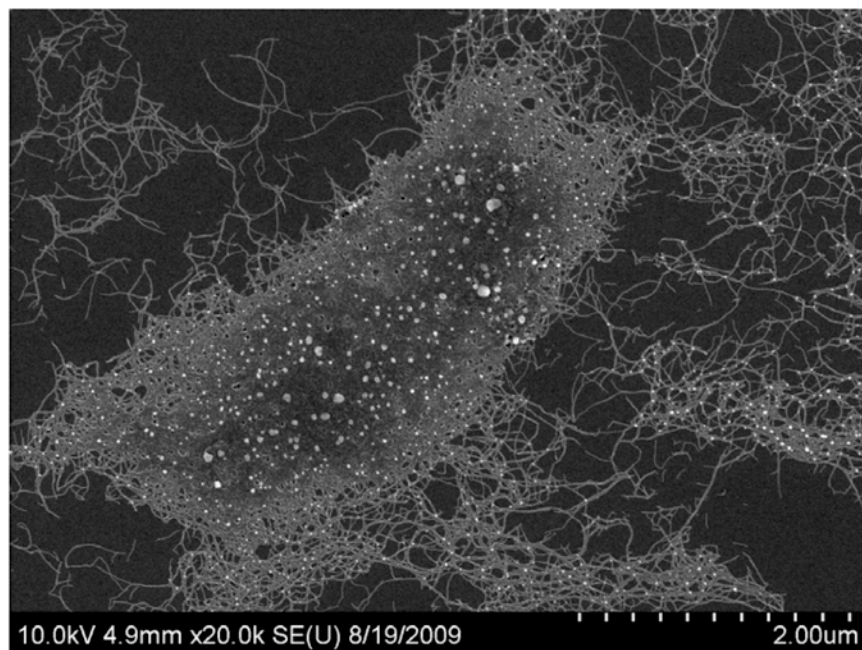


Figure S9E. SEM image of RNTs (50 μM) incubated with H_2AuCl_4 (20 equivalents) $\text{H}_2\text{O}:\text{CH}_3\text{OH}$ (50:50).

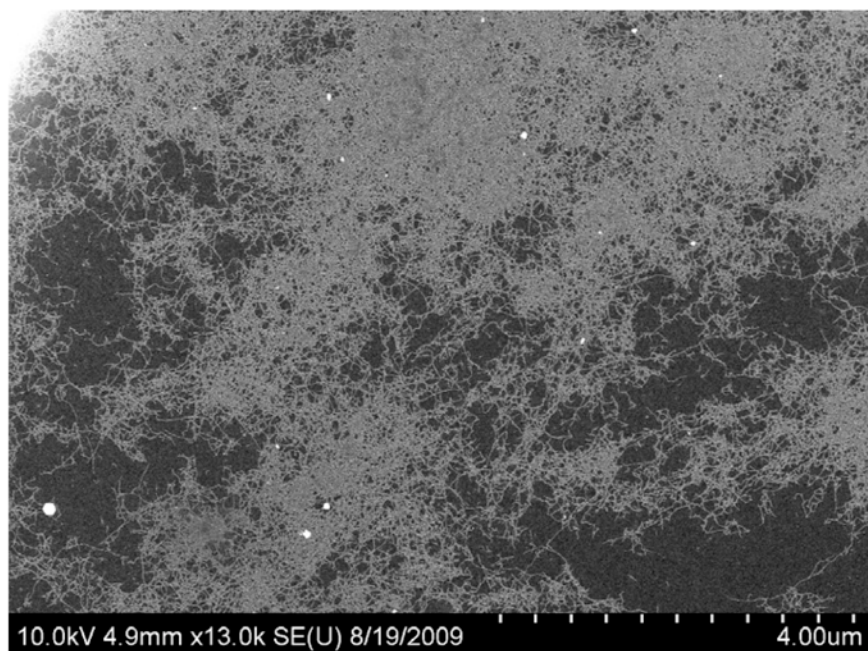


Figure S9F. SEM image of RNTs (50 μ M) incubated with HAuCl_4 (20 equivalents) H_2O :DMSO (75:25).

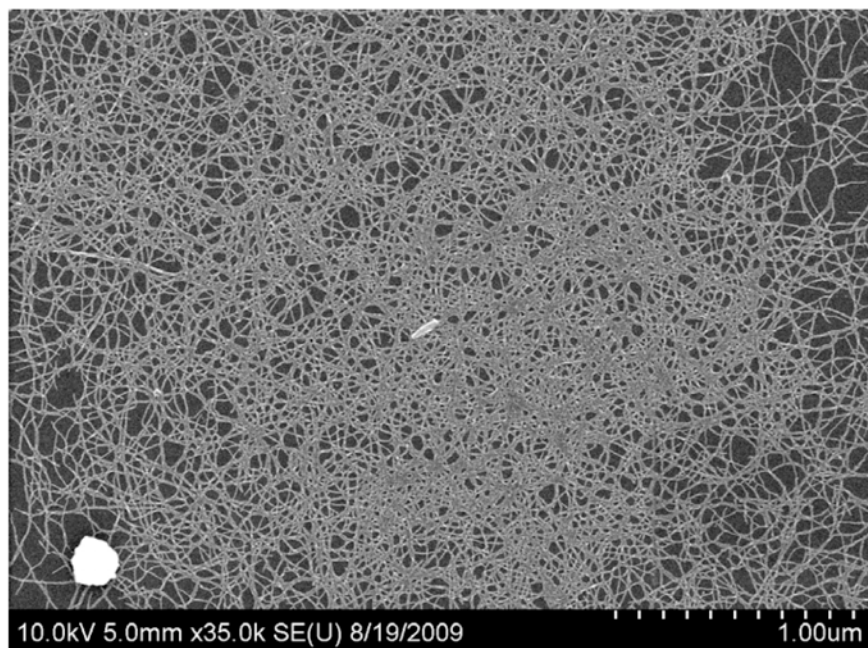


Figure S9G. SEM image of RNTs (50 μ M) incubated with HAuCl_4 (20 equivalents) H_2O :DMSO (50:50).

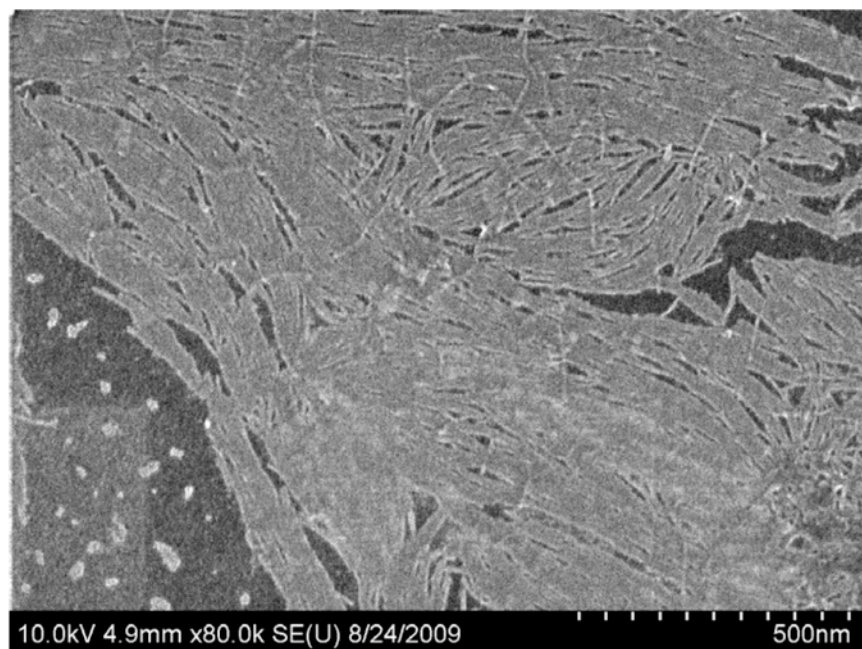


Figure S9H. SEM image of RNTs (50 μ M) with SDS (10 μ L of 1% w/w aqueous solution) followed by incubation with HAuCl₄ (20 equivalents).

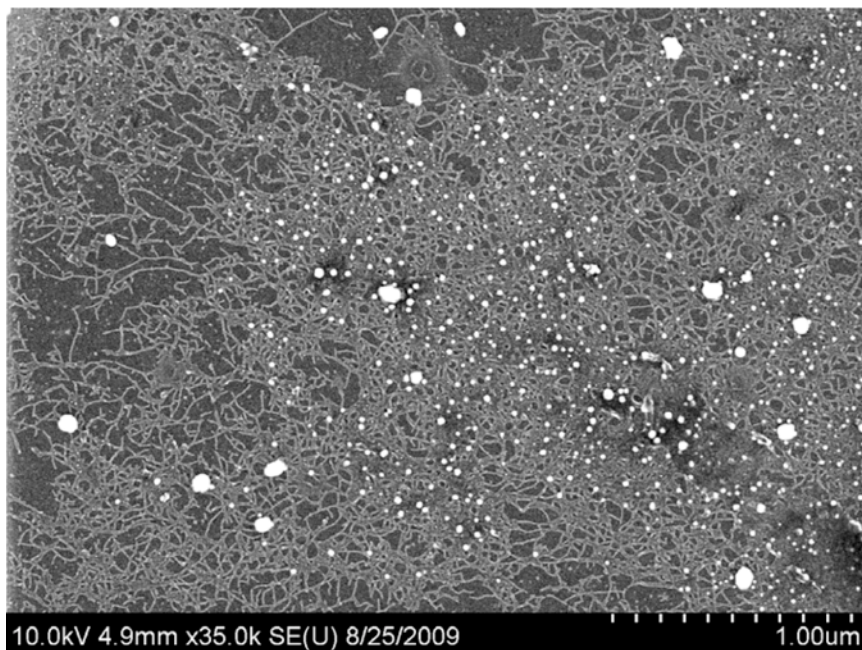


Figure S9I. SEM image of RNTs (50 μ M) with CTAB (10 μ L of 1% w/w aqueous solution) followed by incubation with HAuCl₄ (20 equivalents).

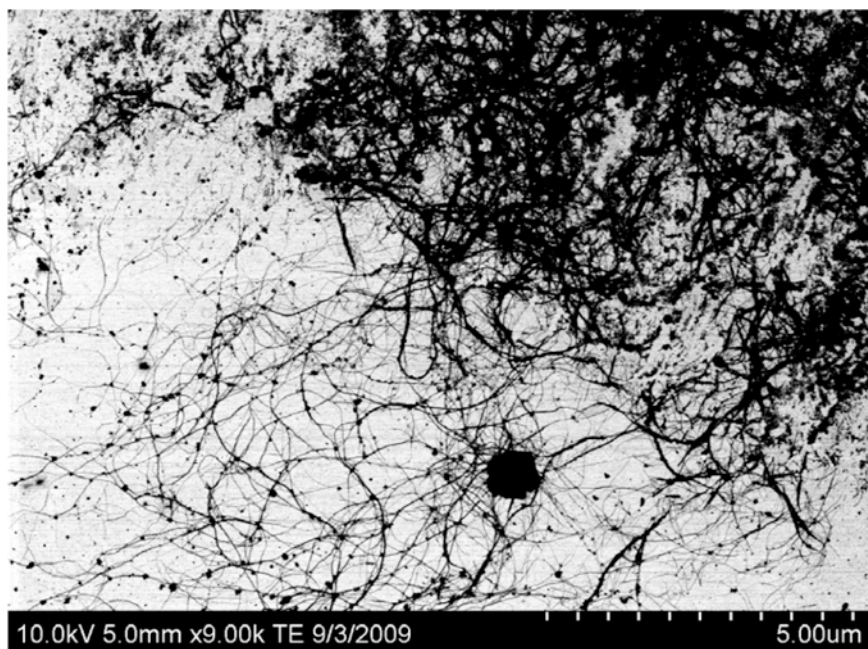


Figure S9J. SEM image of RNTs (50 μM) with Triton X-100 (10 μL of 1% w/w aqueous solution) followed by incubation with HAuCl_4 (20 equivalents).

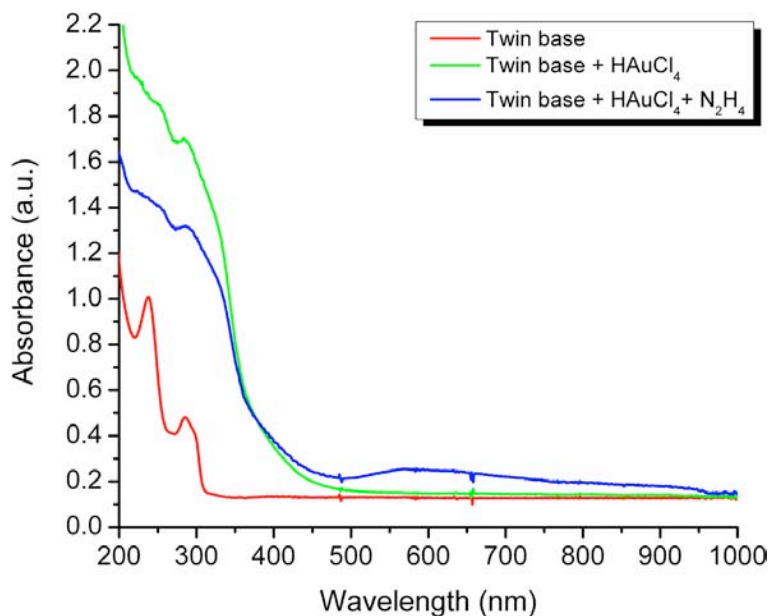


Figure S10. UV-Vis spectra of RNTs with subsequent additions of HAuCl_4 and N_2H_4 . The red trace is a typical UV-Vis spectrum of RNTs (50 μM in water). The green trace is the UV-Vis spectrum of RNTs (50 μM in water) with HAuCl_4 (20 equivalents). The blue trace is the UV-Vis spectrum of RNTs (50 μM in water) with HAuCl_4 (20 equivalents) and N_2H_4 (2 equivalents). The latter spectrum is featureless around 520 nm as the Au NP diameter is <2 nm. The broad peak at 570 nm is most likely the result of the formation of Au NPs aggregate.