Site-Specific Deposition of Au Nanoparticles in CNT Films by Chemical Bonding

*Aruna Velamakanni, Carl W. Magnuson, K. J. Ganesh, Yanwu Zhu, Jinho An, Paulo J. Ferreira, and Rodney S. Ruoff**

Supporting Information

Figure S1 shows the UV–Vis spectra of gold hydrosol (obtained by sodium borohydrate reduction) and also of Au-Cys¹. The strong absorption at 512 nm is the characteristic gold plasmon resonance. The spectra of Au-Cys nanoparticles showed a red shift and broadening of the above band indicating some aggregation as a consequence of surface modification. The interaction of cysteine with the gold nanoparticles was also seen by a rapid change in the color of the solution from ruby red to blue on addition of cysteine to the gold hydrosol.

Figure S1. UV spectra of the gold hydrosol and also of the cysteine capped gold nanoparticles.

FT-IR spectra were employed to in an attempt to detect the characteristic bands of MWCNTs with different groups and also the cysteine moiety after gold nanoparticle conjugation. Figure S2 represents the FTIR spectrum of acid functionalized MWCNTs (MWCNT-COOH). The IR spectrum shows a very small peak at 3500 cm^{-1} characteristic of the -OH stretch region from carboxylic acids. MWCNTs are treated with strong acids ($\text{H}_2\text{SO}_4 + \text{HNO}_3$) to introduce oxidation. The FTIR of acid chloride functionalized MWCNTs (MWCNT-COCl), Figure S3, shows a clear decrease in the intensity of the -OH stretch that indicates the conversion of -COOH groups to -COCl . This is also indicated from XPS data as discussed in the main text. Figure S4 represents the MWCNT-COCl linked with Au-Cys nanoparticles. It shows a characteristic stretch from the amide bond at 3300 cm^{-1} corresponding to the amide bond formed as a result of the linking of cysteine capped gold nanoparticles (Au-Cys) to the MWCNT-COOH (MWCNT-AuCys).

Figure S2. FTIR spectrum of acid functionalized multiwalled carbon nanotubes (MWCNT-COOH).

Figure S3. FTIR spectrum of acid functionalized MWCNTs (MWCNT-COCl).

Figure S4. FTIR spectrum of MWCNTs linked with Au-Cys (MWCNT-AuCys).

The endcaps of the MWCNTs would open if harsh oxidizing conditions, such as high temperature treatment and/or sonication, are used. To prevent this, mild oxidation conditions, such as stirring the MWCNTs in $\text{H}_2\text{SO}_4 + \text{HNO}_3$ (3:1) at room temperature, were used rather than sonication. This approach results in the retention of end caps as seen in the TEM image below (Figure S5 (a-c)).

Figure S5. (a) TEM images showing intact endcaps on oxidized MWCNTs before functionalization with $-\text{COCl}$ groups. The dark spot is not a gold nanoparticle but is due to mass thickness contrast. (b) and (c) show intact endcaps with and without gold nanoparticles respectively. (Scale bars in (b) and (c) are 50 nm.)

Figure S6a shows the comparative XPS survey spectrum of the pristine MWCNTs, MWCNT-COOH and MWCNT-COCl samples. The MWCNT-COOH sample shows an increase in the oxygen peak and the MWCNT-COCl sample shows a peak for Cl 2p indicating that the MWCNT-COOH functionalized tubes have been converted to MWCNT-COCl.

Figure S6b shows the high resolution Cl 2p spectrum of the MWCNT-COCl sample at 199.5 eV that is indicative of a C-Cl bond incorporated due to the formation of CO-Cl bonds.

Figure S6. (a) Comparative survey spectra of as-purchased (dashed), MWCNT-COOH (dotted), and MWCNT-COCl (solid) samples. The MWCNT-COOH sample shows a clear increase in the oxygen content and the MWCNT-COCl sample shows a peak for Cl 2p. (b) The Cl 2p peak at 199.5 eV is indicative of a C-Cl bond that is incorporated due to the formation of CO-Cl bonds.

To determine the percentage of the network occupied by nodes, the length occupied by the nodes was divided by the total length of MWCNTs in the network. Figure S6 shows an example of how these two lengths were measured. To get the fraction of the MWCNTs that are at the network nodes, the length of the nodes was divided by the length of the nodes plus the lengths of the segments of the MWCNTs. Images of networks containing over 100 nodes were analyzed. It was found that 30% of the lengths were at nodes while 85% of the Au-Cys nanoparticles were located at nodes.

Figure S7. TEM image of part of a MWCNT network with gold nanoparticles at a node (image obtained on networks after annealing), where both the segments and nodes of the network could be easily differentiated. The green lines represent the linear length of the MWCNTs occupied by the node and the red lines represent the segments. In this image, 2 of the 3 gold nanoparticles are located at a node (circled).

Figure S8. Transmittance plot of films made from both pristine MWCNTs and MWCNT-Au-Cys. At 550 nm, the transmittance of the pristine MWCNT network is 53.1% and the MWCNT-Au-Cys network is 54.8%.

Figure S9. I-V plots for the thin films made with pristine MWCNTs and MWCNT-Au-Cys before and after annealing. The non-linearities in the curves are an artifact of the characterization setup, not a property of the films. When the current supply changes between the high and low current regimes, the actual current is lower than reported causing dips in the I-V curves. To obtain the sheet resistance the slope of the I-V curve is multiplied by $\pi/\ln 2$ (~4.5). From the slope of these I-V curves, the sheet resistance of the films was determined to be 41 k $\Omega/\square$ for the pristine MWCNT film, 580 k $\Omega/\square$ for the pre-annealed MWCNT-Au-Cys film, and 19.5 k $\Omega/\square$ for the post-annealed MWCNT-Au-Cys film.

Figure S 10 (a and b) shows the TEM images and (c) the SEM image from a control experiment performed to find out if uncapped gold nanoparticles adhere to the MWCNT networks and if adhering, whether they do so in selected regions of the network. The results show that the uncapped gold nanoparticles do not adhere to the network and instead aggregate into larger particles away from the network.

Figure S10. (a) TEM image of gold nanoparticles that were not capped with cysteine. The gold nanoparticles were not attached to MWCNTs and their sizes were both larger and their distribution varied more greatly than the gold nanoparticles capped with cysteine. (b) TEM image of a MWCNT network from the same sample as (a). (c) SEM image of a region of a MWCNT network with non-capped gold nanoparticles. Most of the gold nanoparticles are washed away during filtration in the film making process. A remaining particle is not at a network node.

Figure S11. TEM image of a post annealed MWCNT-COCl-AyCysNP network. Note that the particles' sizes and positions are the same as before annealing.

For **Figure 2b** in the main text, the image quality is limited by factors as mentioned below:

In order to accurately determine the identity of the nanoparticles positioned at the nodes by electron diffraction, sharp spot patterns were achieved by using the 'D-STEM' technique, which employs a near-parallel illumination with a convergence angle less than 1 mrad in a modified STEM configuration. In any scanning transmission condition, the image resolution is determined by the probe size, and the probe size for low probe defining apertures (low convergence angles) depends on the diffraction limit. Therefore, the probe size in D-STEM (for such low convergence at 200 kV) is $\sim 1-2$ nm. The modified STEM optics in D-STEM results in uncorrectable distortions of the off-axis beams during the scanning process.^{2, 3}

These two factors impair the image resolution (in figure 2b). In conventional STEM, operating at convergence angles of the order of 10-20 mrad, the probe sizes are much smaller, which in turn provides better spatial resolution in real space. However in reciprocal space, it results in large discs which also suffer from dynamical diffraction effects and disc overlaps that hinder accurate indexing. D-STEM was used to position the probe accurately at the nanoscale feature of interest in the image and simultaneously obtain easily indexable sharp diffraction patterns which prove the location of the nanoparticles and that they are in fact gold Au (0) nanoparticles.

References

1. Hak Yong, K.; Aryal, S.; Remant, B. K. C.; Dharmaraj, N.; Bhattarai, N.; Chi Hun, K., Spectroscopic identification of S-Au interaction in cysteine capped gold nanoparticles. *Spectrochimica Acta, Part A (Molecular and Biomolecular Spectroscopy)* **2006**, *63*, 160-163.
2. Ganesh, K. J.; Kawasaki, M.; Zhou, J. P.; Ferreira, P. J., A STEM Parallel Diffraction Technique Applied to Nanomaterials *Microscopy and Microanalysis*, Vol. 15, Supplement S2 July **2009**, pp 752-753.
3. Ganesh, K. J.; Kawasaki, M.; Zhou, J. P.; Ferreira, P. J., *Microscopy and Microanalysis*, in review.