NON-DESTRUCTIVE DIFFERENTIATION BETWEEN METALLIC AND SEMICONDUCTING SINGLE-WALLED CARBON NANOTUBES ON SUBSTRATE

N. Kuganathan[a*], **T.-Y. Chen**[b], **Y. X. Thong**[c]
M. B. Chan-Park[c], **E. Bichoutskaia**[a*] and **L.-J. Li**[b*]

[a]School of Chemistry, University of Nottingham, Nottingham, NG7 2RD, UK
[b]Research Center for Applied Sciences, Academia Sinica, Taipei, 11529, Taiwan
[c]School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore, 637459
[*]Corresponding authors: *navaratnarajah.kuganathan@nottingham.ac.uk*,
elena.bichoutskaia@nottingham.ac.uk (theory),
lanceli@gate.sinica.edu.tw (experiment)

Carbon nanotubes represent one of the structural forms of carbon discovered in 1991 by Iijima [1]. Due to their rich mechanical and electronic properties as well as promise in many applications, carbon nanotubes attract considerable research interest. Single-walled carbon nanotube (SWNT) ensembles and networks are potentially useful for high-performance electronic sensor devices and transistors. However, the lack of non-destructive and direct methods for distinguishing metallic and semiconducting SWNTs *directly on substrates* remains major obstacle in the controlled production of SWNT-based logic devices [2].

Recent experimental studies of Dr. Lain-Jong Li *et al* indicate that the Au-coated AFM tip exhibits stronger adhesion force with metallic SWNTs compared with semiconducting ones, thus allowing a simple, fast and non-destructive differentiation between metallic and semiconducting nanotubes using scanning probe microscopy [3]. The adhesion force measurements allow to completely distinguish between metallic and semiconducting SWNTs with the diameter ranging from 1.4 to 1.8 nm (Figure1) since there is no overlap in the force histograms for metallic and semiconducting SWNTs. However, for the SWNTs with smaller diameters (1.0 to 1.4 nm), the Au tip is not able to fully differentiate them, because the adhesion force overlaps in the force region of 7 to 10 nN. Notably, semiconducting SWNTs consistently exhibit low adhesion force (less than 10 nN) regardless of the diameter. By contrast, the adhesion force for metallic SWNTs has a wide distribution. Minor part of the smaller diameter metallic SWNTs exhibit low values of the adhesion force, which overlap with those of semiconducting SWNTs.

We calculate the interaction of gold atom and small gold clusters with metallic and semiconducting SWNTs using Density Functional Theory (DFT) in order to understand the nature and strength of the binding between them. The CASTEP code [4], which solves the standard Kohn-Sham equations using plane wave basis sets, has been employed in all calculations. For the exchange correlation energy term the Generalised Gradient Approximation (GGA) has been used in the form of the Perdew-Burke-Ernzerhof (PBE) functional [5]. Ultrasoft pseudopotentials were generated using the "on-the-fly" formalism in CASTEP.

The optimised configurations of Au atom and the Au_{20} cluster [6] interacting with metallic

(8,8) SWNT and semiconducting (14,0) SWNT are shown in figures 2a-d.
These two SWNTs have similar diameter of about 11 Å. The calculated optimised separations between the cluster (and atom) and SWNTs indicate that the Au - SWNT separation is consistently shorter in the case of the interaction with metallic SWNTs, with particularly significant difference in the separation values for gold atom, which indicates the strong bonding interaction of gold atom with metallic SWNTs. In all cases, larger separation distances were obtained for the interaction with semiconducting SWNTs predicting weaker Au-C interaction. The calculated binding energies confirm that the interaction of Au atom and Au_{20} cluster is stronger with metallic SWNTs than with semiconducting SWNTs. The difference in the strength of the binding becomes more profound for the SWNTs with larger diameters. Mulliken population charge analysis has been carried out to estimate the charge transfer between Au atom and SWNTs. The charge transferred to metallic SWNTs is significantly larger than that to the semiconducting SWNTs, consistently showing that the Au atom has stronger interaction with metallic SWNTs. The calculated density of states (DOS) confirmed the nature of the interaction of gold with metallic SWNTs.
In conclusion, Au exhibits stronger interaction with metallic SWNTs through the charge transfer to SWNTs. The interaction differences between Au-metallic SWNT and Ausemiconducting SWNT can be distinguished by direct imaging of the adhesion force mapping on substrates using scanning probe microscopy. This provides a potentially useful and efficient method for characterization of the electronic type of individually dispersed SWNTs, low-density networks or aligned SWNTs, which have been considered promising in electronic applications.
This computational part of this research has been funded by EPSRC-GB Career Acceleration Fellowship awarded to EB and the High Performance Computing (HPC) facility at the University of Nottingham.

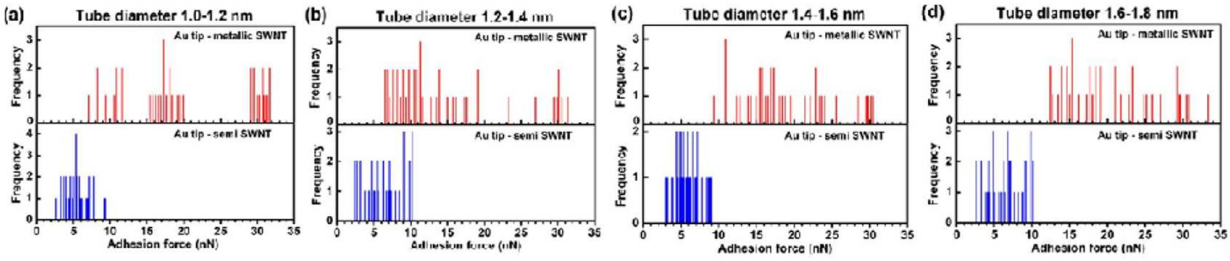

Figure 1: Histograms of the adhesion force for Au tip for different diameter range of SWNT: (a) 1.0-1.2; (b) 1.2-1.4 nm, (c) 1.4-1.6; and (d) 1.6-1.8 nm.

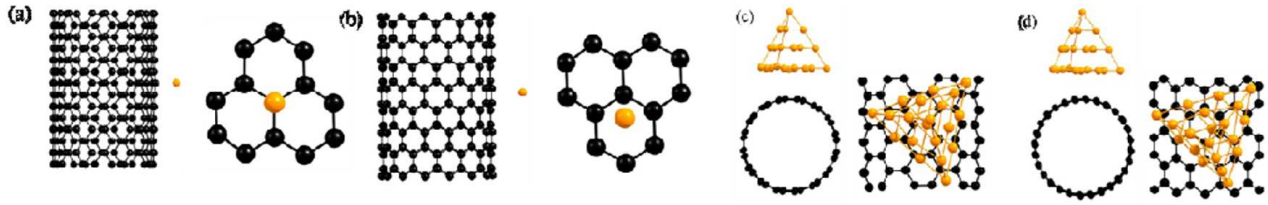

Figure 2: Optimized structures of the interacting systems consisting of (a) Au atom and (8,8) SWNT; (b) Au atom and (14,0) SWNT; (c) Au_{20} cluster and (8,8) SWNT; (d) Au_{20} and (14,0) SWNT obtained using DFT.

References

[1] S. Iijima, Nature, 354 (1991) 36.
[2] Topinka *et al.*, Nano Lett, 9 (2009) 1866.
[3] Tzu-Yin Chen *et al.*, NanoLetters (2011) submitted.
[4] M. C. Payne *et al.*, Rev. Mod. Phys, 64 (1992) 1045.
[5] J. P. Perdew *et al.*, Phys. Rev. Lett, 77 (1996) 3865.
[6] E. S. Kryachko *et al.*, Int. J. Quantum. Chem, 107 (2007) 2922.