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An immunosensor based on N-doped multiwalled carbon nanotubes

Hilary J. Burch, **S. Antoranz Contera**, M. de Planque, K. Voitchovsky and J.F. Ryan

Bionanotechnology IRC, Physics Dept., Clarendon Lab., University of Oxford, Oxford OX1 3PU, UK
Phone: +44-1865-272269 E-mail:s.antoranzcontera1@physics.ox.ac.uk

1. Introduction

Carbon nanotubes (CNTs) combine molecular-scale dimensions with excellent electronic properties offering unique possibilities for chemical and biological sensing. However CNTs biosensor devices can have disadvantages of low conductivity and high contact resistance. CNTs conductance depends on their chirality. At present, it is not possible to synthesize pure carbon nanotubes with the same, predetermined chirality, and therefore known electronic structure and electrical transport properties. However it has been predicted that substitutional doping of NTs with nitrogen or boron provides the possibility of producing a sample of NTs that all have metallic properties, independent of their chirality.

Here we report electrical conductance measurements of nitrogen-doped multiwalled carbon nanotubes (CNx MWNTs). Furthermore the potential of CNx MWNTs for bio applications is investigated by functionalisation of individual nanotubes with proteins of different sizes and charges and monitoring the effect of the adsorption by a combination of spectroscopies and antibody binding assays. Finally we demonstrate the successful development of a CNx MWNTs based sensing device. The devices can detect the binding of different antigens and antibodies. The mechanisms for the detection are investigated.

2. Results and discussion

Electrical conductance of CN_x MWNTs

The basic electronic structure of undoped SWNTs is dependent on their chirality, such that they are either metallic or semiconducting. In metallic SWNTs, two subbands contribute at the Fermi energy (E_F), giving rise to a conductance of $2G_0$ where $G_0=2e^2/h=1/12.9$ kΩ. To test the effect of N-doping on CNTs we have preformed a statistical study of the low-bias conductance values and conductance versus voltage *G-V* curves for both individual CN_x MWNTs and bundles (x=2–5 at. %). The electrical measurements were performed using an AFM z piezo to move a CNx MWNT flake towards a highly ordered pyrolytic graphite (HOPG) electrode keeping the force applied constant during electrical measurements [2]. High conductance ($1.0\pm0.3G_0$) measurements at low bias for individual CN_x MWNTs are demonstrated. Conductance increases linearly with voltage (Fig. 1) at a rate of $0.7\pm0.2G_0$V until the threshold for electrical breakdown is reached. Electrical breakdown of individual CNx MWNTs resulted in a series of discrete steps corresponding to the breakdown of individual MWNT layers. The steps observed were of unequal sizes, in contrast to the equal steps observed for un-doped MWNTs, this is probably due to different concentrations of N in each layer.

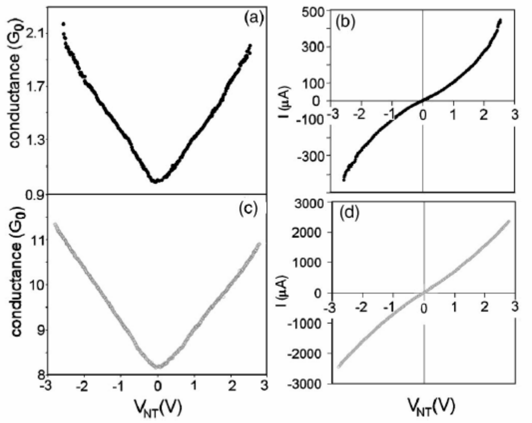

Fig. 1 (a) *G-V* and (b) corresponding *I-V* curve for an individual CN_x MWNT. (c) *G-V* and (d) corresponding *I-V* curve for a CN_x MWNT bundle.

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Functionalization with proteins

Raw and acid-treated CNx MWNTs were functionalized with four different proteins which vary in charge and size: ferredoxin (12 kDa, pI 3.88), ferritin (440 kDa, pI 5.38) and cytochrome c (12 kDa, pI 9.52) and azurin (14 kDa, pI 5.72). To evaluate the effect of CNT adsorption on metalloprotein conformation a systematic characterization of the protein conformation before and after forming the conjugates was performed using AFM, circular dichroism spectroscopy, UV-VIS spectroscopy and antibody binding assays (Fig.2). From the combined results of these three techniques, we conclude that the proteins retain their native conformations when adsorbed to acid-treated CNx MWNTs. The mechanisms of adsorption are investigated

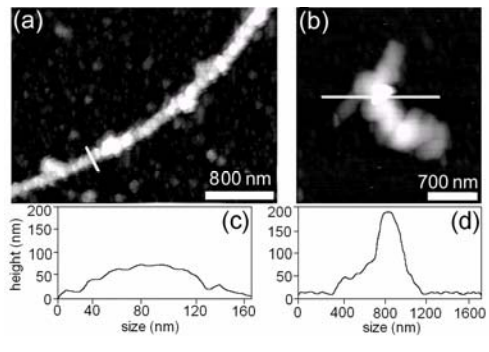

Fig. 2 AC-AFM height images of individual acid-treated CNx MWNTs functionalised with (a) ferritin only and (b)

ferritin/anti-ferritin; (c) and (d) show the corresponding height profiles for (a) and (b) respectively.

Development of a biosensing device

A network of CNx MWNTs is contacted by Au electrodes deposited via an electroless plating method. The devices can sense the binding of ferritin, azurin and cyt c and the additional binding of anti-ferritin and anti-cyt c in real time and in saline aqueous solution (Fig. 3). Additionally, the effect of the ionic strength on the biosensor performance is systematically studied.

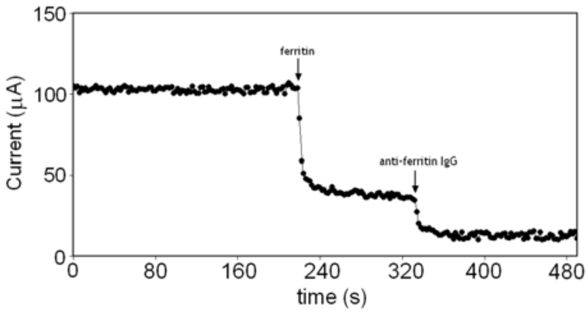

Fig. 3 Real time I-t response of a device to ferritin and then a second response to its specific antibody antiferritin

3. Conclusions

The electrical conductance of individual CNx MWNTs was measured and found have a mean value of 1.0− 0.3 G_0. This result had not been achieved previously, as all measurements of the conductance of CNx MWNTs in the literature reported very low conductances ($0.01G_0$). I-V characteristics of the CNx MWNTs were found to be linear. CNx MWNTs were successfully functionalized with proteins, furthermore using a combination of techniques we demonstrated the correct folding of proteins upon adsorption. Finally a novel immunsensor device based on CNx MWNTs and electroless plating of Au electrodes was developed. The devices can sense the binding of ferritin, azurin and cyt c and also the additional binding of anti-ferritin and anti-cyt c. The mechanisms for the detection have been invetsigated

Acknowledgements

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References

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[2] H.J. Burch, J.A. Davies, E. Brown, L. Hao, S. Antoranz Contera, N. Grobert, J. F. Ryan, Appl. Phys. Lett. **89** (2006) 143110.