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In the Lab

Development of Carbon Based Electrochemical Sensors for Water Analysis

Johnson Matthey Technology Review features new laboratory research

Julie Macpherson is a Professor in the Department of Chemistry at the University of Warwick, UK. Her research focuses on the development of sensors based on different forms of carbon, including conducting diamond, carbon nanotubes and graphene, with a range of applications in environmental monitoring, healthcare technologies and water research. She has published over 150 papers and 14 patents.

About the Researcher

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About the Research

Carbon is an extremely interesting element which can be arranged in different forms, two of which are of interest in the group's research: diamond (sp^3) and carbon nanotubes (sp^2). The group is working towards an electrochemical understanding of the different forms of carbon and how the material can be appropriately structured in order to produce the most efficient sensor for a wide range of applications. As the sensor is often based on electrochemical principles, the material must conduct. For sp^2 carbon this is not a problem; for diamond it is. Hence during synthesis diamond is doped with boron (boron doped diamond (BDD)). At sufficient doping levels the material turns black and electrically behaves as a semi-metal. In the conducting diamond arena, work with the industrial diamond company Element Six has focused on methods to produce BDD electrodes in any geometry, where the electrode component is insulated in diamond; this has led to a variety of solution-based sensing applications. All-diamond electrodes enable the sensor to be placed in extreme or complex environments, where other electrode materials fail, for long periods of time, continuously monitoring. BDD is also extremely robust when subject to high applied potentials, for example, for the production of ozone or other oxidative species in water treatment processes. **Figure 1** shows two examples of all-diamond sensors, from the group.

The use of a dual electrode configuration has been used, for example, as a means of controlling the local pH environment of the sensing electrode.

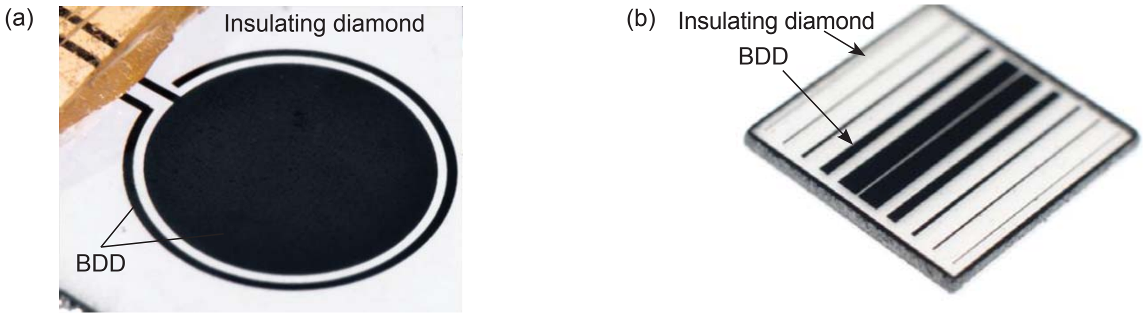

Fig. 1. (a) Ring-disc all-diamond sensor structure. The disc has a diameter of 3 mm; (b) all-diamond multiple band electrode sensor. The width of the diamond chip is ~1 cm × 1 cm. For both images the black tracks are BDD and the transparent areas are insulating diamond (Image copyright Jon C. Newland, University of Warwick, UK)

The outer or upstream BDD electrode (in a fluidic flow cell) can be used to electrochemically break down water, creating a controlled pH environment over the detector electrode to optimise the sensing process of interest. These structures have been successfully deployed to detect heavy metal (for example, mercury) ions and dissolved hydrogen sulfide in water (**Figure 2**) in far from ideal pH conditions. The BDD electrodes can also be combined with other measurement techniques to further enhance analytical capabilities. For example, electrochemical X-ray fluorescence is a recently emerged technique based on BDD electrodes which enables unique chemical identification and quantification of complex 'soups' of metal ions in solution, with the ultimate aim being to measure these directly at the source.

The group is also investigating the electrochemical sensing capabilities of single walled carbon nanotubes (SWNTs), with a focus on healthcare applications. Growth of SWNTs takes place in the laboratory. For trace level analysis, the optimal arrangement in terms of sensitivity, time and cost was a two dimensional network of SWNTs grown directly onto insulating substrates. When incorporated into a suitable microfluidic flow system, these electrodes were shown to be capable of sub-nanomolar detection of dopamine and ferrocene labelled molecules (**Figure 3**) in biologically relevant solutions. Working with high resolution electrochemical imaging techniques it was also possible to elucidate the electrochemical behaviour and sensing capabilities of SWNTs at the single tube level, showing that the entire sidewall is active (**Figure 4**).

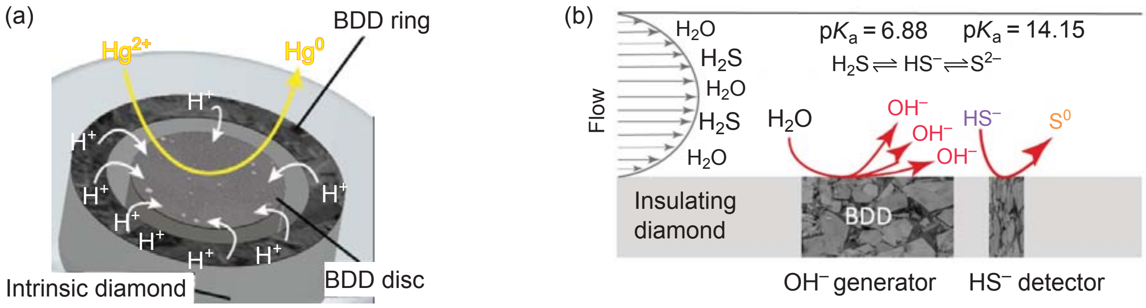

Fig. 2. pH optimisation of a dual detector electrode using two different configurations: (a) generation of H$^+$ by the ring to control the pH environment of the disc (Adapted with permission from T. L. Read, E. Bitziou, M. B. Joseph and J. V. Macpherson, *Anal. Chem*., 2014, **86**, (1), 367. Copyright (2014) American Chemical Society); (b) upstream generation of OH$^-$ in a flow device floods the downstream detector electrode, optimising the pH of the sensor (Reprinted with permission from E. Bitziou, M. B. Joseph, T. L. Read, N. Palmer, T. Mollart, M. E. Newton and J. V. Macpherson, *Anal. Chem*., 2014, **86**, (21), 10834. Copyright (2014) American Chemical Society)

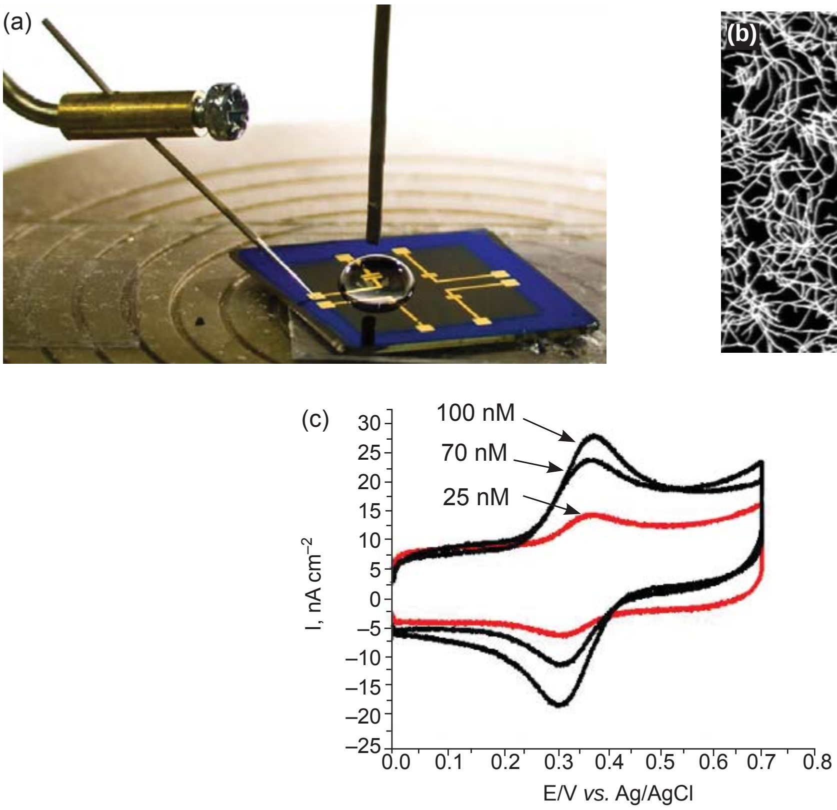

Fig. 3. (a) Optical picture of a SWNT network chip for sensing applications (Image copyright Petr Dudin, University of Warwick, UK); (b) electron microscope image of a SWNT network electrode (10 μm × 10 μm); (c) cyclic voltammogram for $FcTMA^+$ detection – red line shows a detection cyclic voltammogram for 25 nM (Reprinted with permission from P. Bertoncello, J. P. Edgeworth, J. V. Macpherson and P. R. Unwin, *J. Am. Chem. Soc.*, 2007, **129**, (36), 10982. Copyright (2007) American Chemical Society)

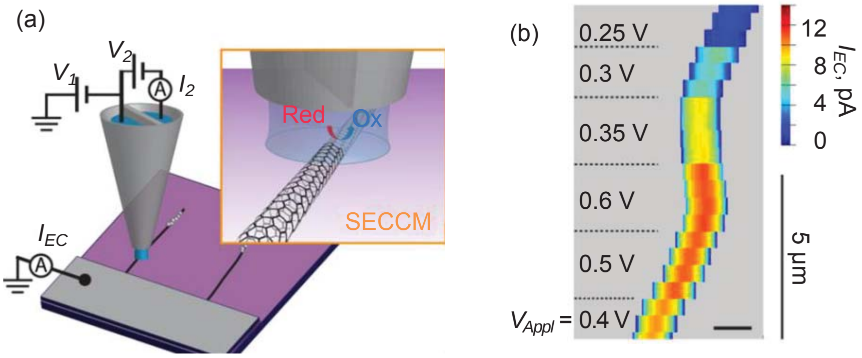

Fig. 4. (a) Set-up for scanning electrochemical cell imaging of a single SWNT; (b) electrochemical image of a single SWNT. As the potential on the SWNT is successively increased the SWNT current increases. The sidewall is shown to be active (Reprinted with permission from A. G. Güell, K. E. Meadows, P. V. Dudin, N. Ebejer, J. V. Macpherson and P. R. Unwin, *Nano Lett.*, 2014, **14**, (1), 220. Copyright (2014) American Chemical Society)

Selected Publications

J. V. Macpherson, *Phys. Chem. Chem. Phys*., 2015, doi: 10.1039/C4CP04022H

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