Modified carbon fiber microelectodes with ruthenium oxide nanoparticles for sensitive detection of nitric oxide in biological samples.

Tiyash Bose, Thomas Bomberger, Mekki Bayachou*

Department of Chemistry, Cleveland State University
2399 Euclid Ave, SR 397, Cleveland, OH 44115

Nitric oxide is an important biological molecule that has diverse functions in human physiology. The concentration of NO in tissues and cells are of vital importance and the presence of too high or too low concentration of this reactive metabolite is the source of a variety of disease states. The major challenges with NO measurement are its low nano-molar concentrations in tissues and short half-life. This calls for the development of a method that is both sensitive and selective for the accurate detection of NO in biological systems. Out of the available analytical methods, electrochemical tools are most promising because they allow for miniaturization of probes as well as direct and accurate detection.

We fabricated the microelectrodes in house using single carbon fibers of 7μm diameter mounted on copper wires, sealed in glass capillaries with 2-mm of the tip exposed. We have developed a method based on electrodeposited ruthenium oxide nanoparticles on the surface of bare carbon fiber microelectrode as a platform for catalytic NO detection. Ruthenium has high affinity for NO and readily forms nitrosyls that can be oxidized electrochemically. This property is one among other reasons that led us to select ruthenium as an electrocatalyst of choice for NO detection.

The electrodeposition of ruthenium oxide nanoparticles is performed in perchloric acid solution containing $RuCl_3$ precursor with constant cycling of the potential at 100 V/s scan rate for 20 minutes as shown in Figure1. Under optimum conditions, the nucleation of ruthenium oxide occurs on the surface of the carbon fiber, with somewhat aligned growth of the nuclei that are in the 100-nm range in diameter as characterized by field emission scanning electron microscopy (FESEM) shown in Figure 2.

Electrocatalytic oxidation of the NO is assessed by cyclic voltammetry and amperometry in standing solutions. The ruthenium-modified microelectrodes exhibit rapid and reproducible response to NO at low applied potential (+0.5V vs. Ag/AgCl). Close analysis of the voltammograms shows that the addition of NO causes the anodic current of the Ru4+/6+ couple to increase with concomitant loss of reversibility. This behavior is a typical signature of an electrocatalytic process triggered by the oxidation of NO. The modified carbon microelectrodes typically show a five-fold increase in sensitivity compared to bare carbon microfibers. Our ruthenium-based NO sensor shows a detection limit in the vicinity of 500 pM, which is orders of magnitude lower than bare carbon fibers. We also show that this modified NO sensor has excellent linearity in relatively a wide range, including very low concentrations of NO. Application of this sensor in analytical measurement of NO in biological samples and at the level of live single cells will be presented and discussed.

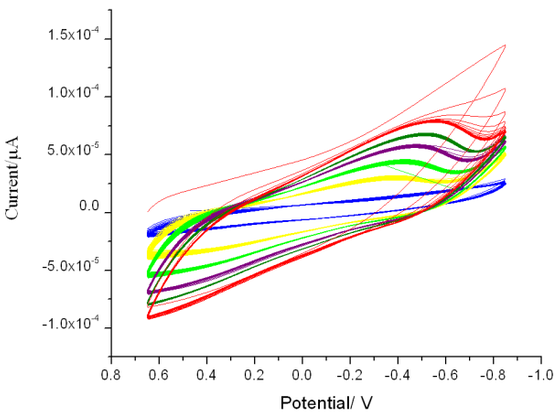

Figure. 1: Typical cyclic voltammograms recorded during the electrodepositon of ruthenium oxide nanoparticles on carbon fiber microelectrode.

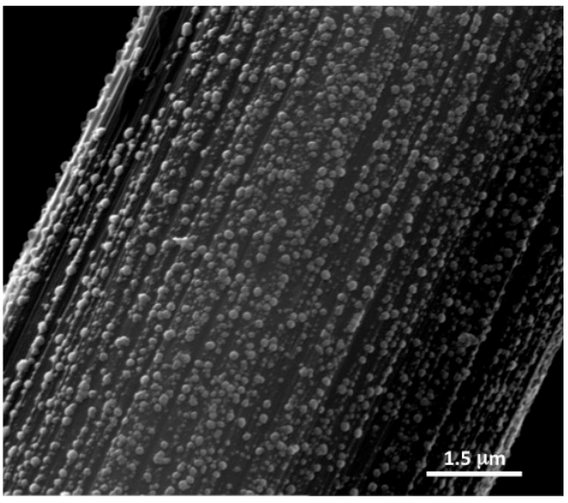

Figure. 2: Ruthenium modified fiber after 20 minutes of electro-deposition as characterized by FESEM.

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