Reduced Graphene Oxide and Single-walled Carbon Nanotubes Composite Material for Electrocatalytic Oxidation of NADH

Tzu-Yen Huang[1,2], Kuo-Chuan Ho[1,3,*], Chih-Wei Chu[2,4,*]

[1] *Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan*
[2] *Research Center for Applied Sciences, Academia Sinica, Taipei 11529, Taiwan*
[3] *Institute of Polymer Science and Engineering, National Taiwan University, Taipei 10617, Taiwan*
[4] *Department of Photonics, National Chiao-Tung University, Hsinchu 30010, Taiwan*

Dihydronicotinamide adenine dinucleotide (NADH) is one of the main charge carriers in cells. The electrochemical detection for NADH has received considerable interest because of its significance both as a cofactor for dehydrogenase enzymes and its role in the electron-transfer chain in biological systems [1].

The electrochemical behavior of a bare glassy carbon electrode (GCE) and electrodes modified with reduced graphene oxide (rGO), single-walled carbon nanotubes (SWCNT), and rGO/SWCNT composites have been comparatively investigated by the cyclic voltammetry (CV) at the scan rate of 20 mV s^{-1} in N_2 saturated PBS. Fig. 1 reveals that the bare GCE exhibited no obvious redox peaks in the potential range between –0.6 and +0.6 V. In contrast, the rGO/SWCNT modified electrode exhibited a well-defined redox couple with a formal potential of –40 mV (*vs.* Ag/AgCl) and the electrochemical properties contributed from the rGO and the SWCNT. Although the rGO exhibited excellent two-dimensional conducting properties, the gaps between the rGO impeded charge transfer. The SWCNT plays a role in connecting the isolated rGO, after blending it with the rGO. Therefore, the composite material shows the superior conductivity and electrochemical property.

We continued to investigate the electrocatalytic activity of modified electrodes toward NADH (Fig.(2)). The electrodes coated with individual and rGO/SWCNT composite films were tested against NADH up to a concentration of 4.0 mM. The peak current for NADH oxidation at the rGO/SWCNT composite film was greater than those of the individual films and the oxidation current was linear upon varying the concentration of the analyte.

Fig. 3 shows the amperometric i–t responses at rGO/SWCNT film modified rotating disc GCE into N_2-saturated PBS. The electrode potential was held at 0.1 V. For every 50 s, the analytes were successively injected into PBS. It is noticed that the rGO/SWCNT film shows a rapid, well-defined amperometric response. The inset also reveals a good relationship between the response current and the concentration of NADH in the range from 0.02 to 0.4 mM. The sensitivity at the rGO/SWNCT modified electrode was 204 μA mM^{-1} cm^{-2} and the limit of detection of NADH was 0.078 μM. Thus, the rGO/SWCNT modified electrode exhibited a high electrochemical response for the detection of NADH–a desirable feature for effective electrochemical sensors. Besides, the interference test reveals that the addition of 0.1 M SO_4^{2-}, Na^+, K^+, or I^- did not interfere significantly for NADH detection.

In summary, we provided a simple method for the detection of NADH by the rGO/SWCNT composite material and further characterized by CV and i–t curves.

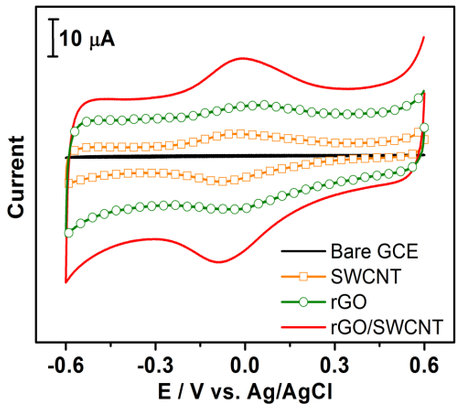

Fig 1. CV of bare GCE and GCEs modified with SWCNT, rGO and rGO/SWCNT composite films in PBS (pH 7.0).

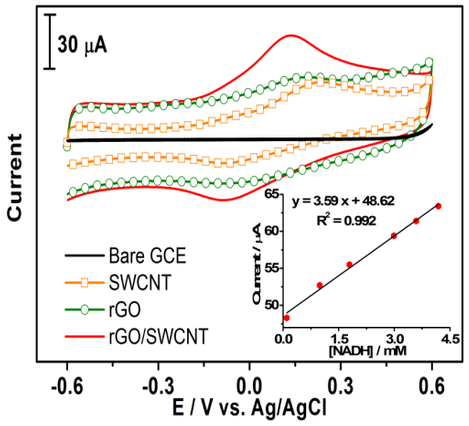

Fig 2. CV of NADH (4.0 mM) at GCEs modified with SWCNT, rGO, and rGO/SWCNT composite films in PBS at 50 mV s^{-1}.

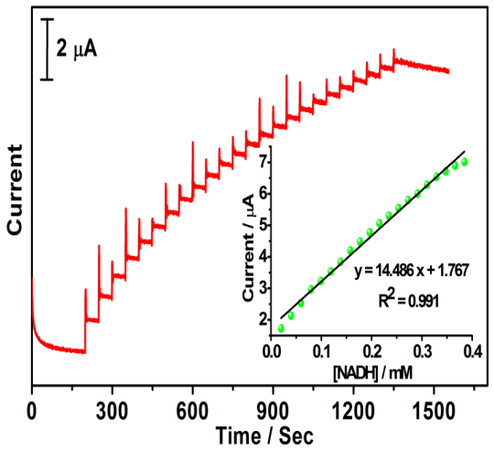

Fig 3. The amperometric i–t responses at a GCE modified with the rGO/SWCNT film after successive additions of NADH (0.02–0.4 mM) into N_2-saturated PBS.

Acknowledgment
We thank the National Science Council of Taiwan and Academia Sinica, Taiwan for financial support.

Reference

[1] Y.Y. Sun, et al, Biosens. Bioelectron., **39**, 289–295 (2013)