PS-7-20 (Late News) Extended Abstracts of the 2019 International Conference on Solid State Devices and Materials, Nagoya, 2019, pp885-886

NH_2-MWCNT/ZnO Nanocomposite as Effective Electrode Material for the Electrochemical Detection of Morin

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Abstract

This report reveals a novel electrochemical sensor for the sensitive and selective determination of morin, a flavonoid with various health-promoting and therapeutic activities. The morin sensor is based on a screen printed carbon electrode (SPCE) modified with a nanocomposite consisting of amine-functionalized multi-walled carbon nanotube (NH_2-MWCNT) and hierarchical rose-like ZnO structure assembled from porous nanosheets. The electrochemical behavior of the prepared NH_2-MWCNT/ZnO/SPCE was evaluated with cyclic voltammetry (CV) and differential pulse voltammetry (DPV), and the electrode exhibits excellent electrocatalytic activity towards the oxidation of morin because of the synergistic effects of NH_2-MWCNT and ZnO. Under optimal conditions, the NH_2-MWCNT/ZnO/SPCE sensor shows a linear response range from 0.2 to 27.4 μM, excellent sensitivity of 2.71 $\mu A \mu M^{-1} cm^{-2}$ and very low limit of detection (LOD) of 0.002 μM. The selectivity of the proposed morin sensor in the presence of common interfering species has also been verified.

1. Introduction

Flavonoids are naturally occurring polyphenols widely found in fruits, vegetables, tea, medicinal herbs and various plant parts. These natural compounds are well known for their health benefits, such as anti-oxidative, anti-inflammatory, anti-mutagenic, and anti-carcinogenic properties. [1] They have found applications in nutraceutical, pharmaceutical, medicinal and cosmetic sectors. Morin is one of the most common flavonol (a subclass of flavonoids) found in plants of the Moraceae family, including mulberry and fig. Researches have shown that morin exhibits various pharmacological and therapeutic activities, including anti-inflammatory, anti-neoplastic, anti-inflammatory, anti-cancer, and anti-viral effects, as well as protection against cardiovascular diseases. [2] Morin also displays strong anti-oxidative activity because of its ability to scavenge reactive oxygen species (ROS), to inhibit enzymes involved in ROS production, and to chelate low valent metal ions such as Fe^{2+} and Cu^{2+}. [3]

The quantitative determination of morin is thus of great interest. Various analytical methods have been used for the detection of morin, including nuclear magnetic spectroscopy (NMR), chromatographic techniques (HPLC), capillary electrophoresis, fluorescent spectroscopy, and electrochemical analyses. Among these, electrochemical approaches provide the advantages of superior sensitivity, fast response, improved selectivity, and low detection limit.

For this purpose, we synthesized a novel nanohybrid composed of amine-functionalized multi-walled carbon nanotube (NH_2-MWCNT) and hierarchical rose-like ZnO. The nanocomposite (NH_2-MWCNT/ZnO) was subsequently applied as the electrode material for the development of morin sensor. A green aqueous solution method was first used to prepare the rose-like ZnO structure, which was then hybridized with NH_2-MWCNT through a simple sonochemical method. The as-prepared NH_2-MWCNT/ZnO nanocomposite was then used to modify screen printed carbon electrode (SPCE) and evaluated for the detection of morin. The proposed morin sensor shows wide linear range with excellent sensitivity and selectivity.

2. Results

Using a two-step process, we synthesized a novel nanohybrid composed of NH_2-MWCNT and hierarchical rose-like ZnO. The rose-like ZnO structure was synthesized using a green aqueous solution method. As shown in Fig. 1A, the rose-like ZnO structure is assembled from porous nanosheeets (Fig. 1B). The rose-like ZnO structure was then composited with NH_2-MWCNT (Fig. 1C) through a simple sonochemical method to form the NH_2-MWCNT/ZnO nanohybrid (Fig. 1D).

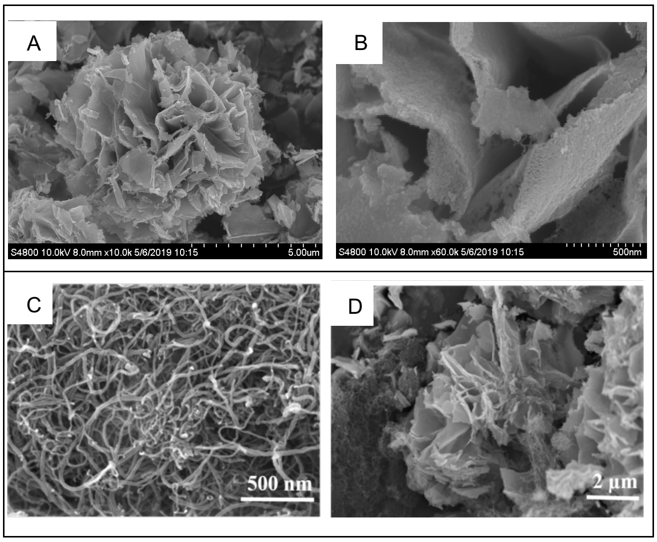

Fig. 1 SEM images of hierarchical rose-like ZnO (A and B), NH_2-MWCNT (C), and NH_2-MWCNT/ZnO nanocomposite (D).

The as-synthesized rose-like structure was subjected to XRD analysis and the results are presented in Fig. 2. All the diffraction peaks are well indexed to the hexagonal wurtzite structure of ZnO (JCPDS card number 36-1451). No other diffraction peaks were observed, suggesting that the high purity of the prepared ZnO nanostructure.

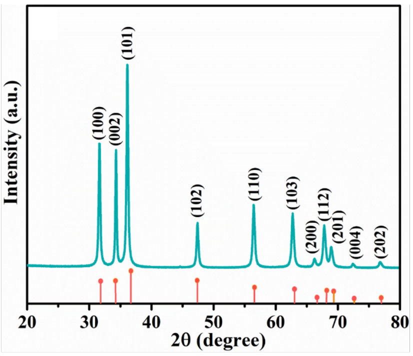

Fig. 2 XRD pattern of the hierarchical rose-like ZnO.

The NH_2-MWCNT/ZnO nanohybrid suspension was drop-casted onto SPCE to form NH_2-MWCNT/ZnO/SPCE sensor, whose electrochemical properties were studied using CV and DPV. Fig. 3 illustrates the electrochemical oxidation of morin on the surface of NH_2-MWCNT/ZnO/SPCE. The quantification of morin was accomplished with the DPV technique. As shown in Fig. 4, the anodic peak current increases linearly with the concentration of morin. Two linear ranges were observed. The low-concentration linear range goes from 0.2 to 27.4 μM with the linear regression equation of I (μA) = $0.5324C_{morin}$ + 3.4881 (R^2 = 0.9817); the high-concentration linear range goes from 43.4 to 803.4 μM with the linear regression equation of I (μA) = $0.0483C_{morin}$ + 18.8478 (R^2 = 0.9985). Based on the slope of the linear regression curve, the LOD of the NH_2-MWCNT/ZnO modified SPCE was determined to be 0.002 μM, with a sensitivity of 2.71 $\mu A \mu M^{-1} cm^{-2}$. The selectivity of NH_2-MWCNT/ZnO/SPCE was evaluated by the DPV technique in the presence of 50 μM morin and excess concentrations of interfering species. As revealed by Fig. 5, these interfering species did not show significant effects toward the detection of morin.

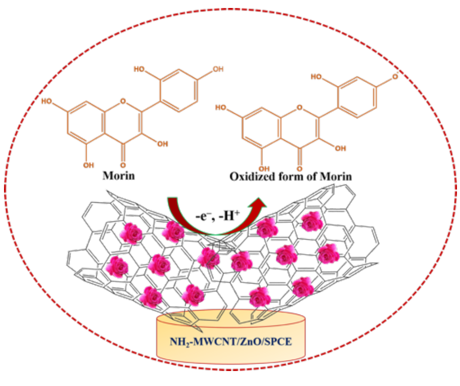

Fig. 3 Scheme showing electrochemical oxidation of morin on the surface of NH_2-MWCNT/ZnO/SPCE.

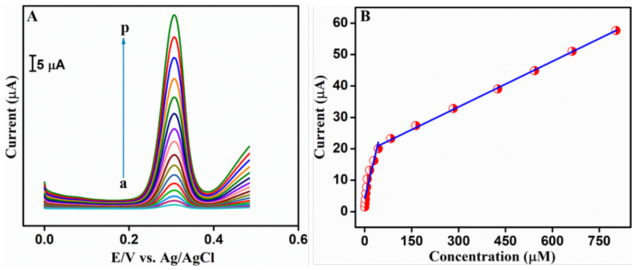

Fig. 4 DPV curves at NH_2-MWCNT/ZnO/SPCE for different concentrations of morin in 0.05M PB solution (pH 7.0) at the scan rate 100 mVs^{-1} (A). Linear plot of cathodic peak current and concentration of morin (B).

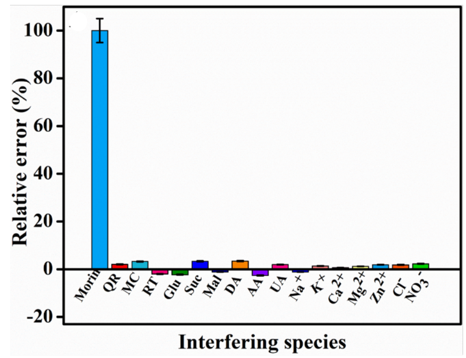

Fig. 5 Interference investigation of NH_2-MWCNT/ZnO/SPCE.

3. Conclusions

An electrochemical sensor based on NH_2-MWCNT/ZnO modified SPCE was developed for the sensitive and selective determination of morin, which is a flavonoid with many health-promoting and therapeutic activities. The quantitative determination of morin was achieved using the DPV technique, which gave a wide linear response range, excellent sensitivity, low LOD, and superior selectivity.

Acknowledgements

We would like to express sincere thanks to Ministry of Science and Technology, Taiwan, R.O.C., for financial support under the Grant MOST 107-2221-E-027-035.

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