Development of PtRu/Graphene Bimetallic Catalysts for H_2O_2 Detection in Biosensing

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Hydrogen peroxide (H_2O_2) is an essential product of many enzymatic reactions which are catalyzed by oxidase enzymes. Hence, H_2O_2 involves in various enzymatic reactions for biomarker detections. Platinum is commonly used to be catalyst. Among platinum based bi-metallic catalysts, PtRu catalyst exhibits a superior activity in detection of H_2O_2. The atomic structure of the carbon supports is a crucial factor in influencing the catalytic activity of PtRu toward the detection of H_2O_2.[1] Carbon based materials are therefore considered as the supporting materials for PtRu catalyst in the the detection process. In this study, Vulcan XC-72R carbon and graphene were used as the supporting materials for the PtRu catalysts.

The PtRu was synthesized using the approach of borohydride reduction. Fig. 1(A) showed the typical amperometric responses of the Nafion/PtRu/GCE, Nafion/ PtRu/Vulcan XC-72R carbon/GCE, and Nafion/PtRu/ Graphene/GCE for continual additions of H_2O_2 at an applied potential of 0.32 V. GCE represents a glassy carbon electrode. It required less than 10 s to achieve 95% steady state current for the catalysts with carbon supported materials. The fast response was due to the facile diffusion of H_2O_2 in the nanocomposite film. In Fig. 1(B) the amperometric response currents vs H_2O_2 concentrations were compared for the three electrodes. The experimentally measured maximum detectable H_2O_2 concentration was found to be 5 mM with a signal-to-noise ratio of 3. This was the average of three measurements, corresponding to each hydrogen peroxide concentration. PtRu/Graphene/GCE showed the best performance when the concentration of H_2O_2 reached 5 mM. This result suggested that PtRu/ Graphene/GCE had good diffusion property due to the fast electron transfer.

As shown in Fig. 2, the calibration was linear over a H_2O_2 concentration range 0.005–0.02 mM: the linear regression equation was I (μA cm^{-2}) = 1019.7 (μA mM^{-1} cm^{-2})C (mM) + 2.72 (μA cm^{-2}) with a coefficient of determination (R^2) = 0.999. The sensitivity and the detection limit were 1019.7 μA mM^{-1} cm^{-2} and 0.185 μM respectively. The detection limit was calculated based on signal to noise ratio (S/N = 3). The performance or reproducibility remained because of the stability of the catalysts. The higher LOD of the Nafion/Graphene/ GCE was attributed to the nanocatalyst having a higher electrocatalytic activity. Additionally, the stability of this catalyst reduced the interference of background current to achieve the high LOD.

Fig. 3 showed the STEM images for the PtRu, PtRu/C, and PtRu/Graphene catalysts. PtRu particles with rather uniform dispersions were formed on the catalysts depending on the different carbon supported materials. In the STEM images of PtRu, an aggregation of particles was observed. This was because pure PtRu particles were not separated without carbon supported materials. Additionally, it appeared that the PtRu particles were more uniformly well-dispersed with Vulcan XC-72 carbon and graphene. This was due to the availability of more surface area of the carbon supported materials, which can facilitate better dispersion of the PtRu particles.

In summary, PtRu particles were more uniformly well-dispersed with Vulcan XC-72 carbon and graphene than pure PtRu catalyst. The PtRu/Graphene catalyst showed the excellent sensitivity and lower detection limit of H_2O_2.

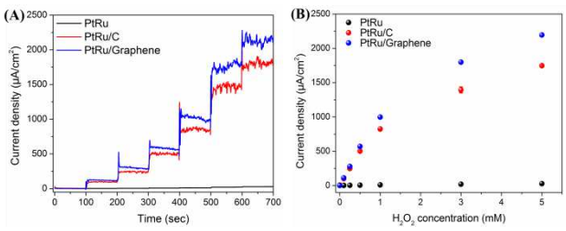

Fig. 1. (A) Amperometric responses to successive additions of H_2O_2. (B) Plots of chronoamperometric currents vs H_2O_2 concentrations for different catalysts.

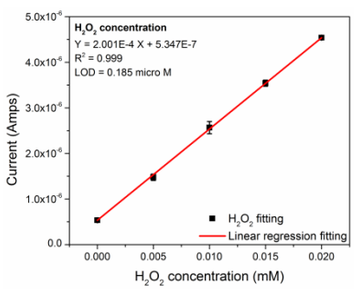

Fig. 2. Calibration curve of the Nafion/PtRu/Graphene/ GCE for H_2O_2.

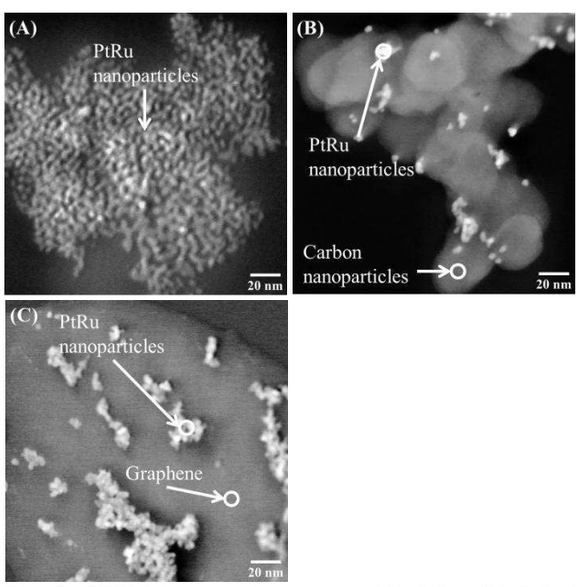

Fig. 3. STEM images of catalysts: (A) PtRu (B) PtRu/ Vulcan XC-72R carbon (C) PtRu/Graphene.

Acknowledgments
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References

[1] K. J. Chen, K. C. Pillai, J. Rick, C. J. Pan, S. H. Wang, C. C. Liu, B. J. Hwang, Biosens. Bioelectron. **2012**, 33, 75-81.