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Synthesis of $ZnMn_2O_4$ microspheres for electrochemical sensing of hydrogen peroxide

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Abstract:
In this work, $ZnMn_2O_4$ microspheres (ZMO-MSs) were synthesized by solvothermal method. The synthesized microspheres were characterized by X-ray diffraction, scanning electron microscopy, energy-dispersive spectroscopy and X-ray photoelectron spectroscopy. The ZMO-MSs exhibited excellent electro-reduction performance towards H_2O_2 in alkaline media. The ZMO-MSs modified glassy carbon electrode was investigated by cyclic voltammetry and amperometry. Linear amperometric responses for H_2O_2 was obtained in a wide range from 0.02 to 15 mM with detection limit of 0.13 μM and high sensitivity of 277.1 mA $mM^{-1}cm^{-2}$. The proposed sensor was successfully applied for the determination of H_2O_2 in milk, indicating a promising platform for practical applications.

Key words: porous $ZnMn_2O_4$ microspheres, H_2O_2 reduction, amperometry.

Introduction

Due to the strong oxidizing and reducing properties, hydrogen peroxide (H_2O_2) has been widely applied in the field of environmental degradation, food, medicine, textile and chemical industries [1,2]. However, considerable electrochemical H_2O_2 sensors are fabricated based on enzymes, which always suffers from disadvantages of loss of enzyme activity [3]. Therefore, it is highly desirable to fabricate enzyme-free sensing platform for H_2O_2 monitoring. Herein, $ZnMn_2O_4$ microspheres (ZMO-MSs) were synthesized by solvothermal method and considered as an efficient way to facilitate the electron transfer at the interface. As a result, the ZMO-MSs exhibited excellent electro-reduction performance towards H_2O_2 in alkaline media.

Preparation of ZMO-MSs

The synthesis of ZMO-MSs followed previous work by Wang [4]. $MnCl_2 \cdot 4H_2O$ (0.396 g), $ZnCl_2$(0.613 g) and urea (0.300 g) were dissolved in 40 mL ethylene glycol. Then, the solution was transferred into a clean Teflon-lined autoclave. After the autoclave was heated to 200 ℃ for 24 h, the product was collected by filtration and washed with deionized water and ethanol several times, followed by drying in vacuum at 60 ℃. Finally, the sample was calcined at 600 ℃for 2 h in air to produce ZMO-MSs.

Characterization of ZMO-MSs by scanning electron microscopy

Scanning electron microscopy is a type of electron Microscope that images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern. Fig. 1 shows morphology of ZMO-MSs. As can be seen from Fig. 1, the size of ZMO-MSs is about 2 μm in diameter.

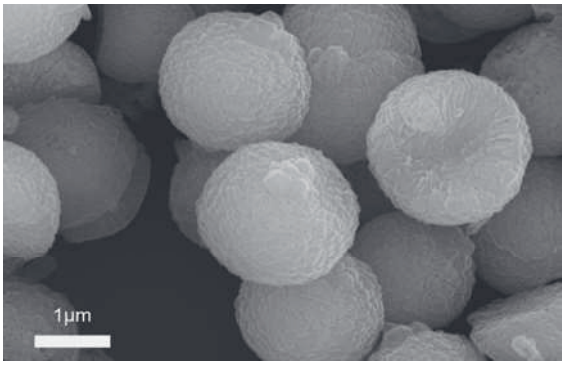

Fig.1. Scanning electron microscopy *image of* ZMO-MSs.

Electrochemical property of ZMO-MSs

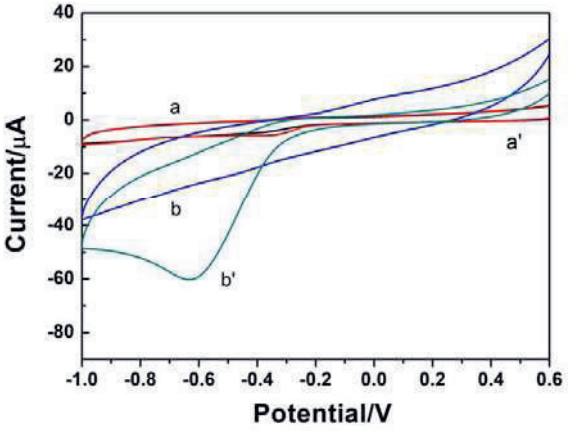

Fig.2. CV curves of the bare GCE (a), ZMO-MSs /GCE without H_2O_2 (a')， ZMO-MSs /GCE (b') in the presence of 1.0 mM H_2O_2 in 0.2 M NaOH (scan rate of 50 mV/s).

The electrocatalytic activity of ZMO-MSs modified electrode (ZMO-MSs/GCE) for H_2O_2 reduction was investigated using a typical three-electrode setup. Fig.2 shows the CVs of bare GCE and ZMO-MSs /GCE toward the reduction of 1mM H_2O_2 in the potential range from 0.6 to −0.1 V. It can be seen that ZMO-MSs/GCE exhibits an excellent catalytic performance for H_2O_2 reduction.

The amperometric responses of ZMO-MSs/GCE with different concentrations of H_2O_2 are shown in Fig. 3. The result showed that the ZMO-MSs/GCE exhibited excellent electrocatalytic property towards H_2O_2 reduction over a wide range of 0.02−15 mM (Fig. 3B) with detection limit of 0.13 μM. The non-enzyme biosensor was successfully applied to the detection of H_2O_2 in milk sample with satisfactory recovery.

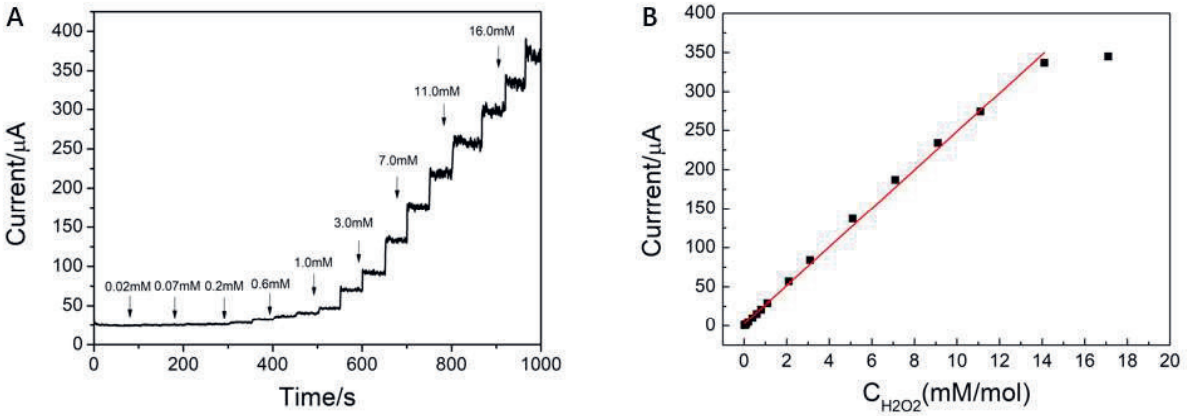

Fig.3. (A) Amperometric responses of the ZMO-MSs/GCE on successive addition of various concentrations of H_2O_2, (B) The corresponding calibration curve in the H_2O_2 concentration range of 0.02–15 mM.

Conclusion

In this work, $ZnMn_2O_4$ microspheres have been successfully synthesized by a facile solvothermal procedure for the application of non-enzymatic electrochemical H_2O_2 sensor with high sensitivity and low detection limit.

Acknowledgements

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