Synthesis of ZnMn$_2$O$_4$ microspheres for electrochemical sensing of hydrogen peroxide

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Abstract:
In this work, ZnMn$_2$O$_4$ 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$_2$O$_2$ in alkaline media. The ZMO-MSs modified glassy carbon electrode was investigated by cyclic voltammetry and amperometry. Linear amperometric responses for H$_2$O$_2$ 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$_2$O$_2$ in milk, indicating a promising platform for practical applications.

Key words: porous ZnMn$_2$O$_4$ microspheres, H$_2$O$_2$ reduction, amperometry.

Introduction
Due to the strong oxidizing and reducing properties, hydrogen peroxide (H$_2$O$_2$) has been widely applied in the field of environmental degradation, food, medicine, textile and chemical industries [1,2]. However, considerable electrochemical H$_2$O$_2$ 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$_2$O$_2$ monitoring. Herein, ZnMn$_2$O$_4$ 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$_2$O$_2$ in alkaline media.

Preparation of ZMO-MSs
The synthesis of ZMO-MSs followed previous work by Wang [4]. MnCl$_2$·4H$_2$O (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 °C 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 °C. Finally, the sample was calcined at 600 °C 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.
Electrochemical property of ZMO-MSs

The electrocatalytic activity of ZMO-MSs modified electrode (ZMO-MSs/GCE) for H$_2$O$_2$ 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$_2$O$_2$ 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$_2$O$_2$ reduction.

The amperometric responses of ZMO-MSs/GCE with different concentrations of H$_2$O$_2$ are shown in Fig. 3. The result showed that the ZMO-MSs/GCE exhibited excellent electrocatalytic property towards H$_2$O$_2$ 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$_2$O$_2$ in milk sample with satisfactory recovery.

Conclusion

In this work, ZnMn$_2$O$_4$ microspheres have been successfully synthesized by a facile solvothermal procedure for the application of non-enzymatic electrochemical H$_2$O$_2$ sensor with high sensitivity and low detection limit.

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References


