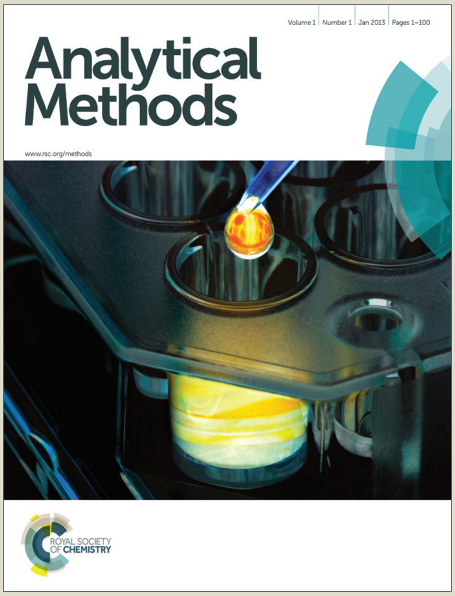
Analytical Methods



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Eelectrochemical hydrogen peroxide sensor based on electrospun $La_{0.7}Sr_{0.3}Mn_{0.75}Co_{0.25}O_3$ naonofibers modified electrode

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Abstract: Electrochemical detection of hydrogen peroxide in alkaline solution was performed on $La_{0.7}Sr_{0.3}Mn_{0.75}Co_{0.25}O_3$ (LSMCO) nanofibers modified carbon paste electrode. Perovskite-type oxide LSMCO nanofibers were prepared by electrospinning and calcination. The morphologies, structures, and electrochemical behaviour of the nanofibers were characterized by scanning electron microscope, energy dispersive spectrometer, X-ray diffraction and cyclic voltammetry. The modified electrode shows excellent electrocatalytic activity towards hydrogen peroxide. Under optimal conditions, the linear response was obtained in the range of 0.5–1000 μM, with high sensitivity and low limit of detection.

Keywords: Electrochemical; Hydrogen peroxide; Nanofibers; Electrospun

1. Introduction

The accurate and rapid determination of hydrogen peroxide (H_2O_2) is of great importance because it is not only a by-product of many highly selective oxidases but also an essential compound in food, pharmaceutical, clinical and environmental analyses [1-4]. A number of techniques have been used for the detection of H_2O_2, such as titrimetry [5], fluorescence [6], spectrophotometry [7], chemiluminescence [8] and

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electrochemistry [9]. Among these methods, electrochemistry has been extensively applied based on a simple and low-cost electrode. Many electrochemical techniques make use of horseradish peroxidase (HRP) to construct H_2O_2 sensors with high selectivity and sensitivity [10-12]. However, the instability, high cost of enzymes and complicated immobilization process restrict the application and development of the enzyme biosensor [13]. In order to solve these problems, considerable attention has been paid to develop nonenzymatic sensors. Various materials used in H_2O_2 enzyme-free sensors, including metal nanoparticles [14,15], metal oxide nanoparticles [16-18], carbon-based materials [19,20] and metal hexacyanoferrates [21].

With the development of nanotechnology, nanomaterials have become excellent substitutes for peroxidase [22]. In particular, nanofibers have received great interest because of their large surface to volume ratio, small diameter, low density and high porosity [23,24]. Many methods have been applied to synthesis nanofibers, such as self-assembly [25], template synthesis [26], stretch method [27] and phase separation [28]. Compared with these methods, electrospinning has proved as a simple, low-cost and versatile way to mass fabricate uniform and continuous nanofibers [29]. The electrospinning apparatus has three major components: a high-voltage power supply, a spinneret and a grounded collector. A high-voltage electric field of several kilovolts is formed between the spinneret and collector. When the electric field overcomes the surface tension of the droplet, a charged liquid of polymer solution is ejected and produces nanofibers on the collector [30].

Perovskite-type oxides have an ideal formula of ABO_3, where A is usually a rare-earth cation, and B is general a transition metal cation. They are well known for their ferroelectric and dielectric properties. when A-site cations partially substituted for divalent cations like Ca^{2+}, Sr^{2+} and Ba^{2+}, equal amount of Mn^{3+} will get converted to Mn^{4+} after doping [31]. Among these compounds, lanthanum strontium manganites ($La_{1-x}Sr_xMnO_3$) has found applications in solid oxide fuel cell [32], gas sensors [33] and environment remediation [34]. When Mn ion is substitute by other transition metals, it will gives rise to changes in the Mn^{3+} and Mn^{4+} ratio, and then alter the magnetic coupling between these ions [35]. $La_{0.7}Sr_{0.3}Mn_{0.75}Co_{0.25}O_3$ (LSMCO) nanofibers are synthesis by electrospinning in this work.

In this work, perovskite-type oxide LSMCO nanofibers were prepared by electrospinning and calcination, and the electrochemical detection of H_2O_2 was performed on LSMCO nanofibers modified carbon paste electrode. The morphologies, structures, and electrochemical behavior of the samples were characterized by scanning electron microscope (SEM), energy dispersive spectrometer (EDS), X-ray diffraction (XRD) and cyclic voltammetry (CV). The proposed LSMCO modified electrode presented a wide linear range, high sensitivity and rapid response for the detection of H_2O_2.

2. Experimental

2.1 Chemicals and reagents

Polyvinyl pyrrolidone (PVP, Mw = 1,300,000) and $Mn(Ac)_2\cdot 4H_2O$ were obtained from Aladdin reagent Co., Ltd. (Shanghai, China). $La(NO_3)_3\cdot nH_2O$,

$Sr(NO_3)_2$, $Co(Ac)_2 \cdot 4H_2O$, N,N-dimethylformamide (DMF), sodium hydroxide, H_2O_2 and graphite powder were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Paraffin oil was bought from Sangon Biotech Co., Ltd. (Shanghai, China). Ultrapure water (resistivity = 18.2 MΩ cm) was used throughout the experiments, and all chemicals were analytically pure.

2.2 Preparation of LSMCO nanofibers

LSMCO nanofibers were prepared using the electrospinning method followed by calcination. To prepare the precursory solution for electrospinning, the total weight of 0.5272 g metal salts (the molar ratio of $La(NO_3)_3 \cdot nH_2O$, $Sr(NO_3)_2$, $Mn(Ac)_2 \cdot 4H_2O$ and $Co(Ac)_2 \cdot 4H_2O$ is (0.7 : 0.3 : 0.75 : 0.25) and 10 wt% of PVP (0.5272 g) were dissolved in 5 mL DMF, followed by stirring 24 h. The obtained gel was loaded into a plastic syringe and connected to the high-voltage power supply for electrospinning. The applied voltage was 15 kV and the collection distance between the spinneret and the collector was 15 cm. After that, the as-prepared $La(NO_3)_3/Sr(NO_3)_2/Mn(Ac)_2/Co(Ac)_2$/PVP composite nanofibers need desiccation in drying oven at 75 ℃ for 12 h. The LSMCO nanofibers were finally obtained by calcining the composite nanofibers in air at 750 ℃ for 2 h with a heating rate of 2 ℃ min^{-1}.

2.3 Preparation of LSMCO/CPE

The carbon paste electrode (CPE) was prepared via hand-mixing graphite powder and paraffin oil at the ratio of 3 : 1 (w/w) until a uniformly wetted paste was formed, followed by packing into a glass tube (3.0 mm in diameter) carefully. A copper wire was inserted into the tube to establish electrical contact. The bare CPE was obtained by polishing the surface against weighing paper.

To prepare the LSMCO nanofibers modified CPE (LSMCO/CPE), 1.0 mg LSMCO nanofibers were dispersed in 1 mL double distilled water by ultrasonic agitation to obtain a homogenous suspension. Then, 10 μL of the suspension (1.0 mg mL^{-1}) was dropped on the smooth surface of the bare CPE. Finally, the LSMCO/CPE was dried under an infrared lamp.

2.4 Characterization of LSMCO nanofibers

Synthesized LSMCO nanofibers were characterized using XRD, SEM, EDS and CV. XRD measurements were obtained on Rigaku D/MAX-2200 X-ray diffraction. FSEM characterizations of the sample were performed on a JEOL JSM-6700F microscope (15.0 kV), equipped with OXFORD INCA EDS analysis. CV measurements were performed using a CHI 842B electrochemical workstation, with a conventional three-electrode system. A modified CPE as the working electrode (3 mm in diameter), a Pt electrode as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode, were used in the measurements.

3. Results and discussion

3.1 Structural and morphological characterization

The crystal structure and composition of LSMCO nanofibers were characterized by XRD after heat treatment at 750 ℃. As shown in Fig. 1, the XRD pattern of the sample was indexed well with standard spectrum of JCPDS-510408. The formation of rhombohedral structure was confirmed by the detectable diffraction peaks at 2θ 32.68, 40.36, 46.99, 58.39, 68.62 and 78.13 ° corresponded to the (104), (202), (024), (214), (208) and (128) crystal planes of LSMCO, respectively.

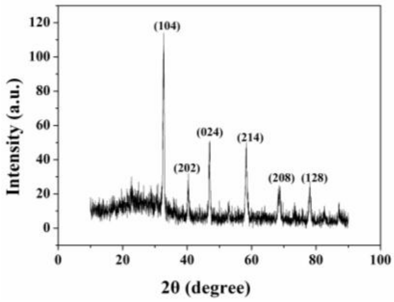

Fig. 1 XRD pattern of electrospun LSMCO nanofibers.

The morphological and structural details of La$(NO_3)_3$/Sr$(NO_3)_2$/Mn$(Ac)_2$ Co$(Ac)_2$//PVP composite nanofibers before and after calcination were investigated by SEM, as shown in Fig. 2. From Fig. 2A, the uncalcined nanofibers had smooth and uniform surfaces with an average diameter of 250-300 nm, and the lengths of these randomly oriented nanofibers could reach several micrometers. Fig. 2B presents the morphologies of LSMCO nanofibers after calcination at 750 ℃ for 2 h. The as-prepared nanofibers had a rough surface and the diameter decreased to approximately 150-200 nm after calcination. These results were related to the evaporation of solvents and the decomposition of PVP backbone during calcination process.

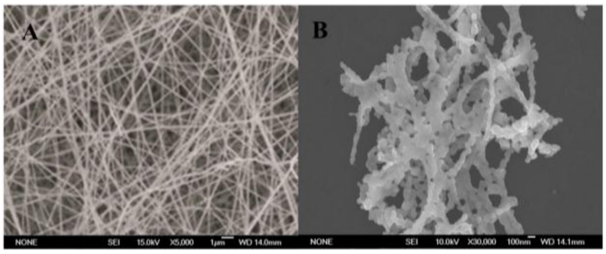

Fig. 2 (A) SEM image of electrospun La$(NO_3)_3$/Sr$(NO_3)_2$/Mn$(Ac)_2$/Co$(Ac)_2$/PVP composite nanofibers; (B) SEM image of electrospun LSMCO nanofibers.

EDS analysis was applied to determine the composition of the as-prepared LSMCO nanofibers (Fig. 3). The EDS spectrum shows the peaks of La, Sr, Mn and Co and O elements. The result shows that the molar ratio of La, Sr, Mn and Co is about 14: 6: 15: 5, suggesting the LSMCO sample was near stoichiometric and conformed to a typical chemical composition of perovskite-typed oxide.

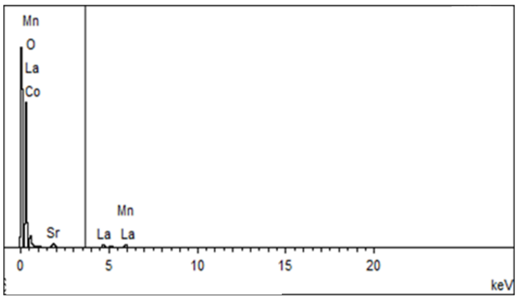

Fig. 3 EDS image of electrospun LSMCO nanofibers.

3.2 H_2O_2 electro-oxidation on LSMCO/CPE

LSMCO nanofibers modified electrodes were investigated towards the direct electrochemical oxidation of H_2O_2 in 0.1 M NaOH alkaline medium. Fig. 4A shows CV behaviors of the bare CPE and LSMCO/CPE in the absence (curve a, c) and presence (curve b, d) of 0.1 mM H_2O_2 e in 0.1 M NaOH at a scan rate of 100 mV s^{-1}. No oxidation/reduction peaks were observed on bare CPE in the absence or presence of 0.1 mM H_2O_2. In contrast, a broad oxidation peak appeared on LSMCO/CPE in 0.1 M NaOH, and the oxidation peak increases after the addition of 0.1 mM H_2O_2. The possible electro-oxidation mechanism of H_2O_2 is given by the following reactions [36]:

$$\mathrm{Mn(IV)Mn(III)} + \mathrm{ne}^- \leftrightarrow \mathrm{Mn(II)} \qquad (1)$$

$$2H_2O_2 - 2e^- \leftrightarrow O_2 + 2H_2O + 2H^+ \qquad (2)$$

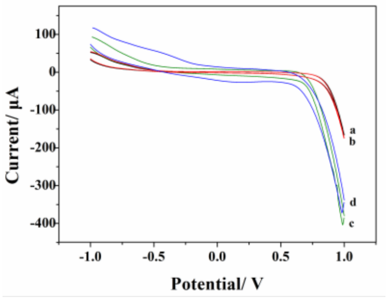

Fig. 4 CVs recorded on the bare CPE and LSMCO/CPE in the absence (a, c) and presence of 0.1 mM H_2O_2 (b, d) in 0.1 M NaOH.

3.3 Optimization of sensing conditions

To improve the electrocatalytic performance of the H_2O_2 sensor, some important influence factors were optimized, including applied potential, the concentration of supporting electrolyte and the concentration of modifier.

Fig. 5A illustrates the effect of the applied potential varying from +0.50 to +0.70 V on the response current of 50 μM H_2O_2 in 0.1 M NaOH solution. From +0.50 to +0.60 V, the current response increased apparently with the increase of applied potential. When the applied potential was higher than +0.60 V, the signal became less stable and the current response tended to decrease. Thus, potential of +0.60 V was choosen for the subsequent studies.

Fig. 5B shows the influence of NaOH concentration in the range of 0.01 to 0.2 M on the amperometric response of 50 μM H_2O_2. The current response of H_2O_2 increased with the increase of NaOH concentration from 0.01 to 0.1 M, and then leveled off. When the concentration was above 0.1 M, the background noise was high, and the current response decreased. Therefore, 0.1 M NaOH was used as supporting electrolyte in all experiments.

The influence of modifier concentrations covered on the surface of electrode was shown in Fig. 5C. The current response enhanced with increasing the concentration of the modifier from 0.5 to 4.0 mg mL^{-1} and reached a maximum value at 2.5 mg mL^{-1}. When the concentration of the modifier increased from 2.5 to 4.0 mg mL^{-1}, the current response decreased obviously. So, 2.5 mg mL^{-1} electrospun LSMCO nanofibers were chosen to prepare the modified CPE.

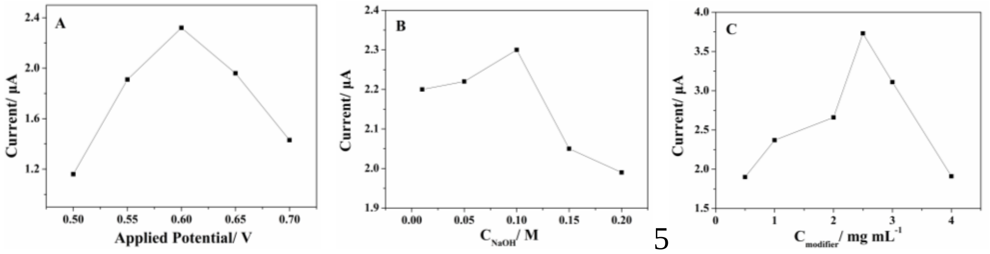

Fig. 5 Effect of experimental conditions on the amperometric response of 50 μM H_2O_2 (A) Applied potential, (B) NaOH concentration, (C) Concentration of LSMCO.

3.4 Amperometric response to H_2O_2 and the calibration curve

Under the optimum conditions, H_2O_2 was detected in 0.1 M NaOH at 0.60 V by the electrode modified with 2.5 mg mL^{-1} LSMCO nanofibers. The amperometric response of the sensor was performed by amperometry (Fig. 6). With the successive addition of H_2O_2 to a continuously stirring NaOH solution, the sensor had a rapid response to the charge of H_2O_2 concentration and obtains steady-state within 5 s. The linear regression equation of current response with H_2O_2 concentration is I (μA) = 0.037 + 0.0969c (μM) (R = 0.998) with a wide linear response range from 0.5 to 1000 μM. The sensitivity of the proposed sensor is 1371.5 μA mM^{-1}cm^{-2}, and the limit of detection is calculated to be 0.17 μM on signal-to-noise ratio of 3. As shown in Table 1, the performance of the present sensor has been compared with some previously reported H_2O_2 sensors [37–41]. These results show that the LSMCO/CPE sensor has a wider linear range and a higher sensitivity.

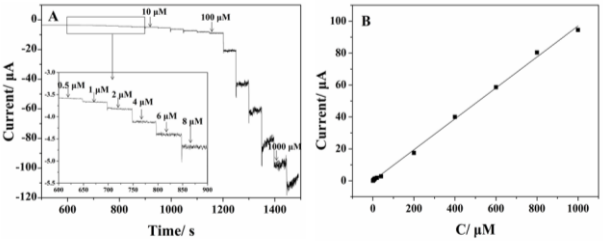

Fig. 6 (A) Current-time curves of LSMCO/CPE at different concentrations of H_2O_2. (B) The calibration curve for H_2O_2 on LSMCO/CPE.

Table 1 Comparison of the performance of the electrospun LSMCO modified CPE with other modified electrodes for H_2O_2 sensors.

Modified electrode	Linear range (μM)	LOD[d] (μM)	Sensitivity ($\mu AmM^{-1}cm^{-2}$)	Ref.
Nano-CuO/CCE[a]	0.78–193.98	0.071	697.0	[37]
Ni/Al-LDHs[b]/GCE	0.036–175	0.009	595.7	[38]
PVA[c]-MWCNTs-PtNPs /GCE	2–3800	0.7	122.63	[39]
Cu_2O nanowires/Au	0.25–5000	0.12	745	[40]
β-MnO_2/GCE	2.5–42900	2.45	307.7	[41]
LSMCO/CPE	0.5–1000	0.17	1371.5	This work

[a] CCE: Carbon ceramic electrode.

[b] LDHs: Layer double hydroxides.

[c] PVA: poly(vinyl alcohol).

[d] LOD: Limit of detection.

3.5 Reproducibility, stability and selectivity of the electrode

The reproducibility, stability and anti-interference are all key properties to the electrochemical sensors and studied by amperometry. Ten successive determinations of H_2O_2 on the same LSMCO/CPE, the relative standard deviation calculated to be 3.46%. The long-term stability was explored by storing the electrode at room temperature for 30 days, and the catalytic current response for H_2O_2 maintains more than 91.8% of its initial value. The anti-interference performance of the sensor was examined by adding other species during the determination of 20 μM H_2O_2. 10 μM AA, DA and UA did not affect the results of determination (Fig. 7).

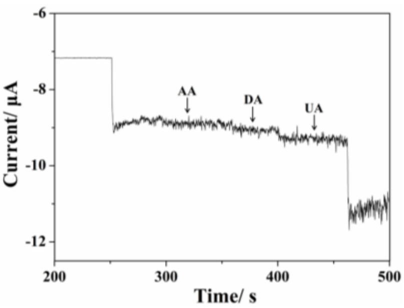

Fig. 7 Amperometric response of LSMCO/CPE with successive additions of 20 μM glucose, 10 μM interferents into 0.1 M NaOH.

3.6 Real sample analysis

In order to verify the practical applicability of the present sensor, LSMCO modified CPE was used to detect H_2O_2 in toothpaste and medical hydrogen peroxide solution. The current-time detection was conducted at 0.6 V applied potential in 0.1 M NaOH, and a magnetic stir was used to create a stirring condition. Standard addition method was applied to get a quantitative determination of the sample. As shown in Table 2 and Table 3, the recoveries of H_2O_2 are obtained, demonstrating that the sensor was effective and satisfactory in real sample determination. The concentration of H_2O_2 in toothpaste sample is 163.0 mg g^{-1}, and the mass fraction of H_2O_2 in medical hydrogen peroxide solution is 2.99 %.

Table 2 Determination of H_2O_2 in toothpaste samples (n = 3).

Sample	Detected (μM)	Added (μM)	Found (μM)	Recovery (%)	R.S.D (%)
1	4.78	3.00	7.92	104.7	2.8
2	5.77	4.00	9.67	97.5	2.3

Table 3 Determination of H_2O_2 in medical hydrogen peroxide solution. (n = 3).

Sample	Detected (μM)	Added (μM)	Found (μM)	Recovery (%)	R.S.D (%)
1	4.38	5	9.25	98.7	2.6
2	8.78	10	19.12	101.8	3.2

4. Conclusion

In conclusion, a novel electrode material composed of LSMCO nanofibers with large surface area and high length-to-diameter was successfully prepared by electrospinning and subsequent calcination. The LSMCO modified electrode exhibited distinctly enhanced electrocatalytic capacity towards H_2O_2. Moreover, the modified electrode was used for H_2O_2 determination with wide linear range, high sensitivity and a low detection limit. The proposed electrospun LSMCO is a promising catalytic electrode material for H_2O_2 sensing, and might be applied in clinical diagnoses, environmental analyses and food industry.

Acknowledgments

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