

Morphological and Compositional Characterization of Electrochemically Active Perovskite Oxides for Sensing Biological Molecules

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Lanthanum based perovskite oxides with the general formula LaBO_3 ($\text{B}=\text{Co}, \text{Ni}, \text{Fe}, \text{Mn}$) are promising electroactive materials, and have been extensively reported as electrodes for supercapacitors, fuel cells, batteries, water splitting, gas sensing, etc., due to the unique characteristics caused by the presence of transition metal at the B-site. [1-5] The electrochemical characteristics of the perovskite structured materials can be improved by inducing the oxygen vacancies and combining different transition metals, resulting a general formula $\text{A}_{1-x}\text{A}'_x\text{B}_{1-y}\text{B}'_y\text{O}_3$ ($\text{A} = \text{La}, \text{Pr}, \text{Gd}, \text{etc.}; \text{A}' = \text{Sr}, \text{Ba}, \text{Ca}, \text{etc.}; \text{B}=\text{B}'=\text{Co}, \text{Ni}, \text{Fe}, \text{Mn}$). [6] Additionally, architecting the size of these materials to the nanoscale domain can increase the electrochemical performance tremendously. Therefore, in the present work, we fabricated $\text{La}_{1-x}\text{Sr}_x\text{B}_{1-y}\text{B}'_y\text{O}_3$ ($\text{B}'=\text{B}''=\text{Co}, \text{Ni}, \text{Mn}$) nanofibers through a sol-gel assisted electrospinning process. The morphological and compositional features of the representative nanofibers were evaluated using an electron microprobe and the sensitivity towards glucose, a common biomolecule, was tested by cyclic voltammetry. $\text{La}_{1-x}\text{Sr}_x\text{Ni}_{1-y-z}\text{Mn}_y\text{Co}_z\text{O}_3$ ($\text{B} = \text{B}' = \text{B}'' = \text{Co}, \text{Ni}, \text{Mn}$) nanofibers were fabricated in three steps: (1) preparation of electrospinnable solution containing the stoichiometric quantities of metal salts and gel-forming medium; (2) fabrication of precursor composite fibers by electrospinning process; and finally (3) calcining the precursor composite fibers above the degradation temperature of the volatile components. The electrospinnable precursor solution was prepared by dissolving 0.07 M of stoichiometric quantities of the metal nitrates in a 20 mL 50/50 ethanol/N,N-dimethylformamide solvent mixture. Then 2.0 g of polyvinylpyrrolidone (PVP) (molecular weight $\sim 1,200,000$ g/mol) was added to the above solution and stirred vigorously for 12 h to ensure uniform mixing. The electrospinning was conducted at atmospheric conditions with an applied voltage of 15 kV, a flow rate of 300 mL/h, and a spinneret to collector distance of 17 cm. The xerogel fibers obtained through the electrospinning process were subsequently calcined at 700 °C in air for 5 h at a ramp of 2 °C/min to get the resulting perovskite nanofibers. Samples were coated with carbon and analyzed in a JEOL field-emission JXA-8530F EPMA, which was equipped with an SDD X-ray energy-dispersive spectrometer (EDS) and five wavelength-dispersive spectrometers (WDSs). The nanofibers was covalently immobilized on a carbon paper electrode surface to be used as a working electrode to detect glucose with cyclic voltammetry in the range of 0.2 - 0.7 Volt (v.s. Ag/AgCl) (CH Instruments Model 440 potentiostat, 3-Electrodes systems: Nanofiber-modified carbon electrode as working, platinum wire as counter, and Ag/AgCl, KCl (1M) as reference electrode). Fig. 1a shows the SEM images of representative $\text{La}_{1-x}\text{Sr}_x\text{Ni}_{1-y-z}\text{Mn}_y\text{Co}_z\text{O}_3$ nanofibers after calcination. A high aspect ratio of the nanofibers with an average size of < 150 nm was observed. The EDS analysis, as shown in Fig. 1b confirmed that the composition of the obtained fibers has significant peaks arising from the respective La, Sr, Co, Ni, Mn, and O elements. WDS analysis was also performed to confirm the elemental composition using different crystals, which was shown in Fig. 2. The sensitivity toward glucose was evaluated by comparing the anodic peak current of the cyclic voltammograms for the representative $\text{La}_{1-x}\text{Sr}_x\text{Ni}_{1-y-z}\text{Mn}_y\text{Co}_z\text{O}_3$ nanofibers, which exhibited a sensitivity of 786 mA/M [7].

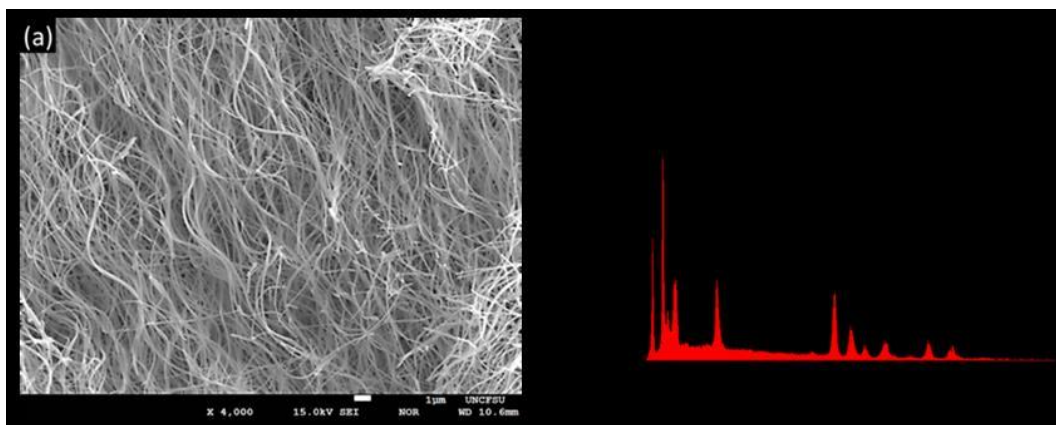


Figure 1. (a) SEM; (b) EDS spectrum of representative electrospun $\text{La}_{1-x}\text{Sr}_x\text{Ni}_{1-y-z}\text{Mn}_y\text{Co}_z\text{O}_3$ perovskite nanofibers.

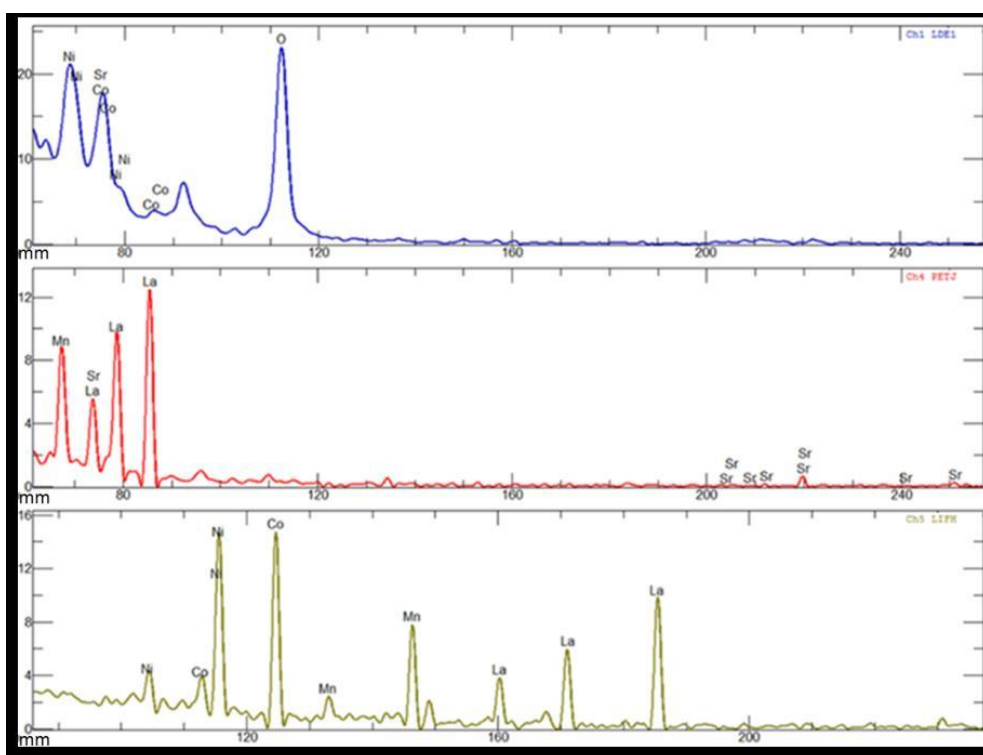


Figure 2. WDS spectra of three crystals of representative electrospun $\text{La}_{1-x}\text{Sr}_x\text{Ni}_{1-y-z}\text{Mn}_y\text{Co}_z\text{O}_3$ perovskite nanofibers.

References

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