

Chemical Microanalysis of SnO₂–MnO₂ Nanofibers in an Electron Probe Microanalyzer

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Tin dioxide (SnO₂) is an N-type semiconductor for a wide range of applications [1]. Hierarchical SnO₂ nanocrystals, in the forms of nanoparticles, nanotubes or nanosheets, have been used for gas sensors [1, 2], supercapacitors [3], lithium-ion batteries [1], and solar cells [1]. With the addition of MnO₂, it was found that SnO₂–MnO₂ nanocomposite powders exhibited remarkable improvement in electrochemical performance of in terms of discharge capacity and low capacity fading, compared with pristine MnO₂ [4]. SnO₂–MnO₂–SnO₂ sandwich-structured structure was also demonstrated to be a high-performance anode in a lithium-ion battery [5]. In this work, we synthesized SnO₂, MnO₂ and mixed SnO₂–MnO₂ nanofibers and conducted microanalysis using an electron probe microanalyzer (EPMA).

Polymer solutions were prepared by dissolving 2.0 g polyvinylpyrrolidone (PVP) (molecular weight ~1,300,000 g/mol) in a 20 mL (50/50) mixture of N,N-dimethylformamide (DMF) with ethanol. Tin chloride (SnCl₂), or manganese chloride (MnCl₂) or a mixture of both, was added to the polymer solution. The electrospinning was conducted at room temperature with applied voltage of 18 kV. The prepared nanofibers were subsequently calcined at 500 °C in air for 5 h to obtain oxide nanofibers. Samples were coated with carbon and analyzed in a JEOL field-emission JXA-8530F EPMA, which was equipped with a SDD X-ray energy-dispersive spectrometer (EDS) and five wavelength-dispersive spectrometers (WDSs), and xCLent IV Hyperspectral Cathodoluminescence System, worked at 10 kV.

Fig. 1(a) shows an SEM image of SnO₂ nanofibers after calcination. The nanofibers become porous, with a diameter of ~150 nm. After calcination, the fibers are in fact composed of small nanoparticles (~50 nm). The EDS analysis, as shown in Fig. 1(b), confirms that its composition is almost stoichiometry of SnO₂. The MnO₂ nanofibers, on the other hand, are composed of large nanoparticles (~150 nm) in the form of chains. Since the melting point of SnO₂ is 1,630 °C while the melting point of MnO₂ is only 535 °C, the MnO₂ nanofibers were melted during the calcination. The EDS spectrum of MnO₂ is shown in Fig. 1(d), with a stoichiometric composition of MnO₂.

The image of mixed SnO₂–MnO₂ nanofibers is shown in Fig. 2(a), with larger diameter (~300 nm) in a porous shape. As shown in Fig. 2(b) from the EDS analysis, the Mn content is very low although the starting molar ratio of Sn:Mn is 1:1, indicating the melting and volatilization of MnO₂ from the mixture during the calcination [6].

References:

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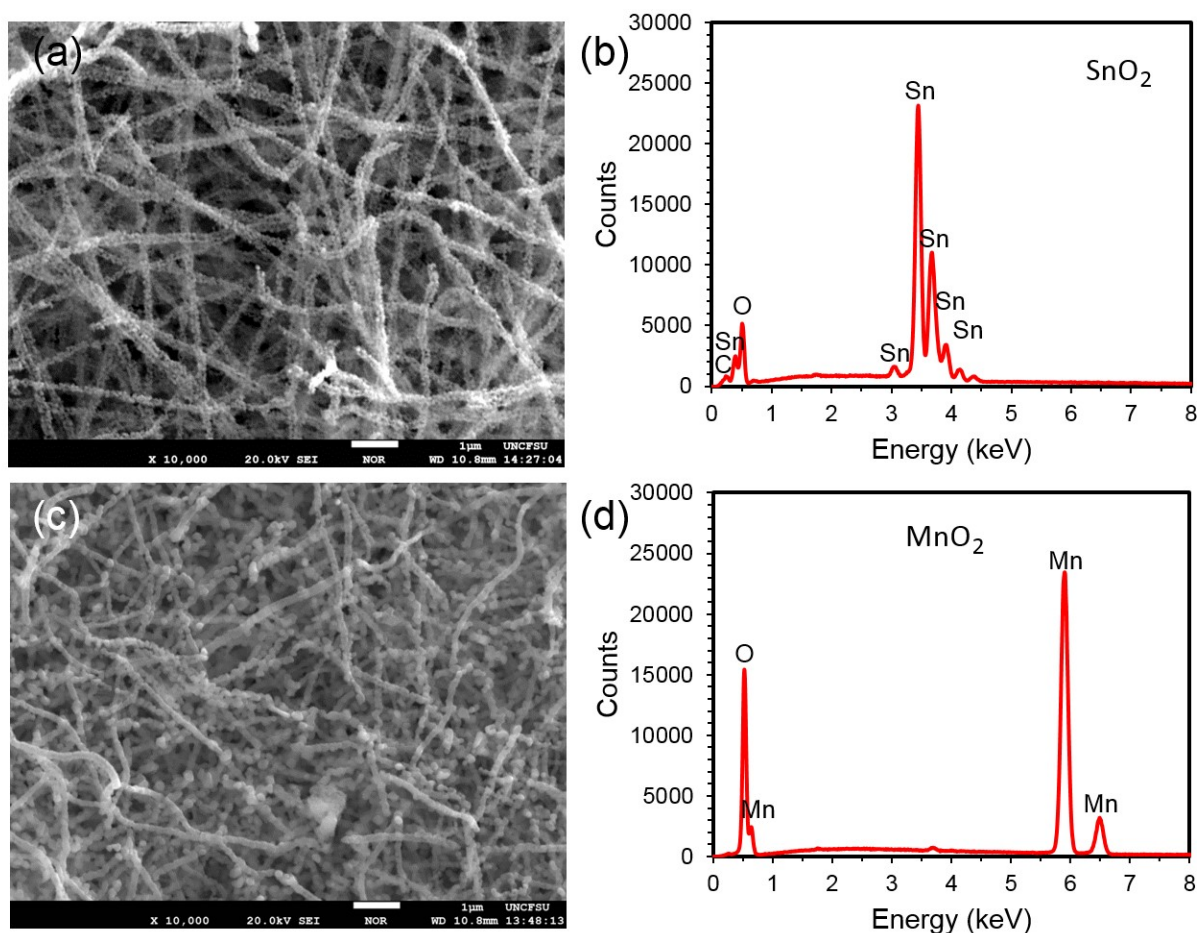


Figure 1. (a, b) SEM image of SnO₂ nanofibers and EDS spectrum; (c, d) SEM image of MnO₂ nanofibers and EDS spectrum.

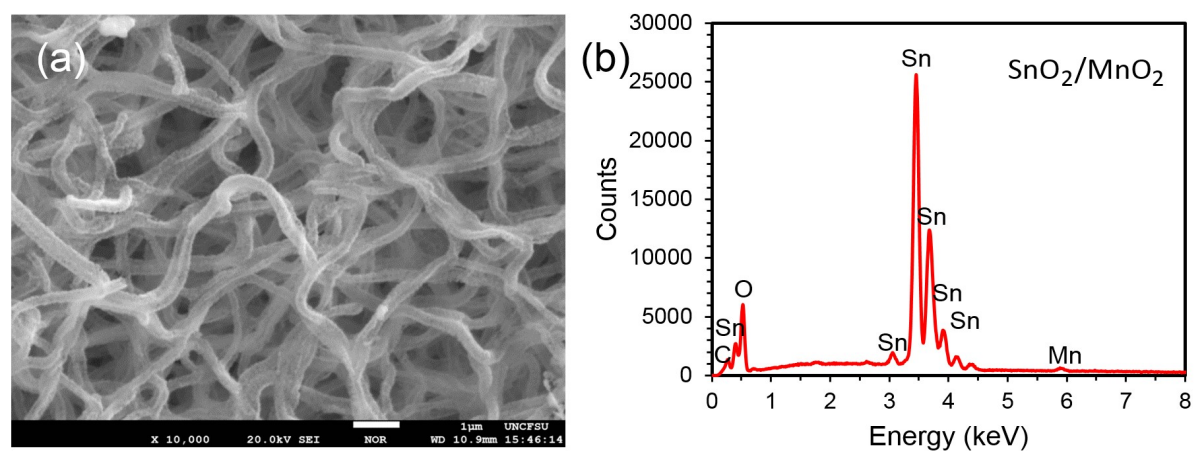


Figure 2. (a) SEM image of SnO₂-MnO₂ nanofibers; (b) EDS spectrum.