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Electrospun CeO_2-ZnO Nanofibers Analyzed by Electron Probe Microanalyzer

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Nanofibers have gained much interest due to their wide range of applications as gas sensors, filters, super-capacitors, solid-oxide fuel cells, and catalysts. Preparation of one dimensional (1D) nanofibers and nanocomposites via electrospinning is a simple technique, which does not require any chemical precursors in the reactions. It is known that ceria (cerium dioxide, CeO_2) possesses a fluorite-type face-centered cubic structure. Such an isotropic structure makes it hard to synthesize 1D material through conventional chemical reactions [1], and thus most of the research on ceria involved nanoparticles. Recently, ceria nanobelts were synthesized by electrodeposition [1], and nanorods by a hydrothermal reaction [2]. However, the nanobelts or nanorods showed limited aspect ratios. Using electrospinning, instead, long ceria nanofibers could be prepared [3]. In this work, we use an electron probe microanalyzer (EPMA) to analyze the ceria nanofibers with chemical dopants.

In the electrospinning process, polymer solutions were prepared by dissolving 0.5 g polyvinylpyrrolidone (PVP) (molecular weight ~1.3×10^6 g/mol) in 8 mL pure ethanol and stirred for 2 h to get viscous solutions. A 0.1 g cerium nitrate hexahydrate, and a mixture of 0.05 g cerium nitrate hexahydrate and 0.05 g zinc nitrate, were fully dissolved into 2 mL deionized water separately, and stirred for 2 h. The Ce- or Ce/Zn-containing solutions were then slowly added into the polymer solution separately and stirred for 1 h. All chemicals were purchased through Sigma Aldrich and were of analytical grades without any further purification. The subsequent solutions were then loaded into a 5-mL plastic syringe with a blunt stainless steel needle (22 gauge), a flow rate of 300−1300 mL/h, applied voltage of 7.5−11 kV and temperature at 30 °C. The prepared nanofibers were subsequently calcined at 480 °C in air for 2 h to obtain metal-oxide nanofibers.

The sample morphologies were characterized using a JEOL 6510 scanning electron microscope (SEM) at 20 kV. All samples were coated with 5 nm of chromium prior to imaging. The as-prepared samples have uniform sizes in the range of 350−500 nm (Fig. 1a−c). It is found that in the samples added with Ce or Ce/Zn, no secondary particles are formed, indicating the metals are uniformly incorporated into the PVP nanofibers. After calcination, the PVP is burned and evaporated, so only oxides remained in the nanofibers with reduced size about 100 nm (Fig. 1d).

In order to analyze the samples in EPMA, the samples must be mounted at the correct height with respect to the wavelength spectrometer (WDS). We deposited thin membranes on a piece of glass slides, and then coated with a carbon film to achieve conductivity. The glass slide reflects visible light for adjusting the sample position. The EPMA analyses were made using a JEOL field-emission JXA-8530F HyperProbe at 15 kV. The WDS shows that Ce and Ce/Zn are uniformly incorporated in the nanofibers. Fig. 2 displays a WDS spectrum of the sample containing Ce and Zn. Quantitative analysis was made using standards of Astimex #32 monazite for Ce, and #46 willemite for Zn. Three spots were analyzed and then accumulated. The quantification yields Ce:Zn = 52.012:47.988, approximately 1:1 in atomic ratio, indicating the Zn has been successfully doped into ceria nanofibers [5].

References

[1] Z.-L. Wang, G.-R. Li, Y.-N. Ou, Z.-P. Feng, D.-L. Qu, Y.-X. Tong. Electrochemical Deposition of Eu^{3+}-Doped CeO_2 Nanobelts with Enhanced Optical Properties. *J. Phys. Chem. C* **115**, 351–356 (2011).
[2] W. Gao, J. Li, X. Zhou, Z. Zhang, Y. Ma, Y. Qu. Repeatable fluorescence switcher of Eu^{3+}-doped CeO_2 nanorods by L(+)-ascorbic acid and hydrogen peroxide. *J. Mater. Chem. C* **2**, 8729–8735 (2014).
[3] D. Fang, M. Zhang, Z. Luo, T. Cao, Q. Wang, Z. Zhou, M. Jiang, C. Xiong. Photoluminescent properties of Eu^{3+} doped electrospun CeO_2 nanofibers. *Opt. Mater.* **38**, 1–5 (2014).
[4] The authors acknowledge funding from the NSF No. 1436120 for this research. The instrumentation at FSU was supported by DoD W911NF-09-1-0011, W911NF-14-1-0060 and W911NF-15-1-0566. C.H. Young is an FSU-RISE scholar.

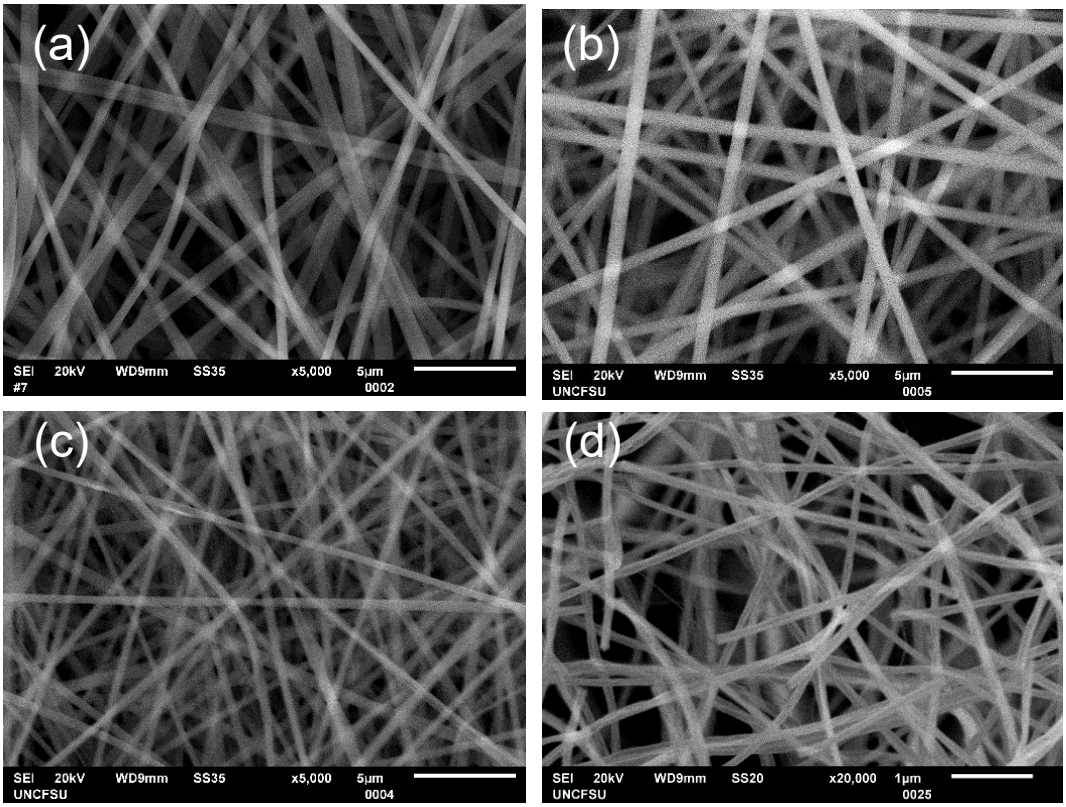

Figure 1. SEM images of nanofibers: (a) pure PVP; (b) PVP with Ce; (d) PVP with Ce and Zn; (d) calcined PVP with Ce sample.

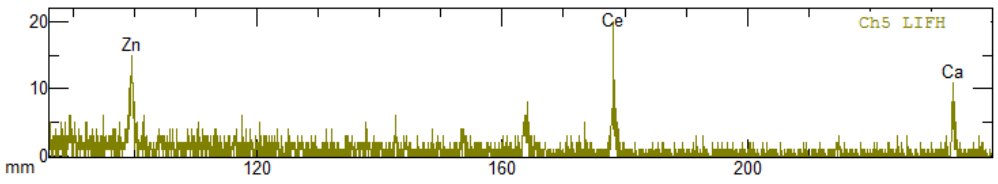

Figure 2. WDS spectrum from the sample of PVP with Ce and Zn (Ca is from the glass slide).

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