The Eurasia Proceedings of Science, Technology, Engineering & Mathematics (EPSTEM)
ISSN: 2602-3199

The Eurasia Proceedings of Science, Technology, Engineering & Mathematics (EPSTEM), 2023

Volume 26, Pages 416-419

IConTES 2023: International Conference on Technology, Engineering and Science

Glycine-Assisted Synthesis of High Surface Area $(FeMnCrCoZn)_3O_4$ Microsheets

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Abstract: To meet the current demands for energy storage and conversion, it is crucial to develop newly designed materials. Porous metal oxides with a high specific surface area and controllable porosity are promising electrode materials for electrochemical energy storage and conversion applications. Furthermore, porous materials offer a unique combination of structural, chemical and physical properties. In this study, porous high-entropy oxides $(FeMnCrCoZn)_3O_4$ were synthesized through soft chemistry route, employing glycine as a pore-forming agent, followed by calcination at various temperatures (500 °C, 600 °C and 700 °C) for 4h. The obtained samples were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. It was observed that the samples were successfully synthesized in porous microsheet morphology and as a single phase in the spinel crystal structure. Additionally, the effect of different calcination temperatures on the pore structure has been investigated.

Keywords: High-entropy oxides, Porous metal oxides, Template-free method

Introduction

Introducing porosity into metal oxides can significantly enhance their performance across various scientific applications, including catalysis (Adegoke &Maxakato, 2022), sensing (Chen et al., 2010), and energy conversion and storage technologies (Veerakumar et al., 2020; Hassan et al., 2021). Materials characterized by a high specific surface area, tunable pore size, and large pore volume play a crucial role in all the aforementioned applications. In fields like batteries and supercapacitors, key factors for effective reversible energy storage include energy density, rate capability, and cycle life. A hierarchically porous structure, featuring interconnected pores across different scales, shortens ion diffusion paths (Liu et al., 2019). This enables deeper electrochemical reactions, thereby maximizing electrode capacity and energy density. Moreover, it facilitates rapid and reversible ion de-intercalation, thereby enhancing rate performance (Liu et al., 2019).

Various chemical techniques (Suzuki et al., 2003; Wu et al., 2020) and physical-chemical methods (Chen et al., 2010) are available for synthesizing materials with hierarchically organized porous structures. Depending on the application of a template and the specific agents used, these approaches can be categorized into soft templating, hard templating, and template-free methods (Wu et al., 2020). Both soft and hard templating methods present challenges for large-scale production due to their high cost and labor-intensive preparation procedures. Ideally, methods devoid of templates are favored for producing hierarchically structured porous materials, featuring sizable pores and diverse shapes (Wu et al., 2020).

In this study, porous $(FeMnCrCoZn)_3O_4$ hierarchical structures were synthesized at different temperatures using the sol-gel based template-free method. The study also investigated how varying heat treatment temperatures affected the phase structure and porosity of the samples.

Method

The equimolar amounts of metal nitrates were dissolved in deionized water and stirred for 30 minutes. Subsequently, glycine (CH_2NH_2COOH) was introduced into the solution, serving as a fuel and chelating agent. Following 2 h of stirring, the solution was transferred onto a Teflon plate and dried overnight at 90°C. The resulting gel structure was subjected to heat treatment in an air atmosphere, with a heating rate of 5°C min^{-1} at 500 °C, 600 °C and 700 °C for 4h to obtain porous $(FeMnCrCoZn)_3O_4$ high-entropy oxide. The X-ray diffraction (XRD) analyses utilized a PANalytical Empyrean diffractometer equipped with Cu Kα radiation, employing a scanning rate of 2° min^{-1}. Sample morphologies were investigated using a ZEISS Ultraplus scanning electron microscope (SEM).

Results and Discussion

Figure 1 displays the XRD patterns for the obtained samples at various temperatures. The peak profiles signify well-crystallized samples in a cubic spinel structure within the Fd-3m space group (96-230-0280 reference card file). No impurities are found under all synthesis conditions. Hence, any significant impact of the synthesis temperature on the formation of the spinel phase is not observed. However, it was observed that the peak intensities increased slightly depending on the temperature, as seen in Figure 1. The lattice parameters of the samples were calculated as 8.3749 Å.

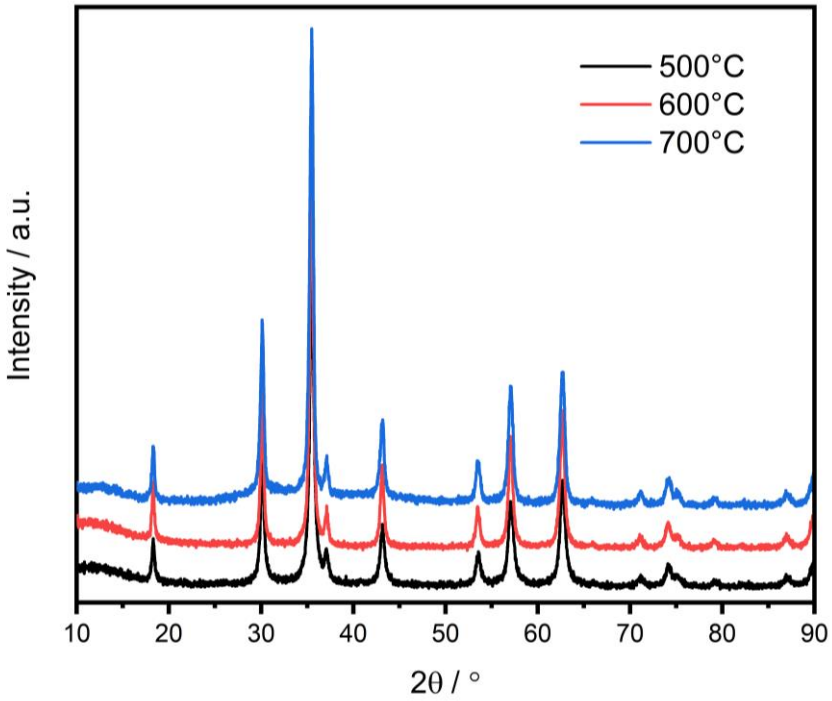

Figure 1. XRD patterns of the synthesized porous HEO samples.

The morphology of the synthesized samples was analyzed by SEM. As can be seen from the images in Figure 2, the samples exhibit a sheet-like and porous structure. This porosity arises from the release of substantial amounts of gas during the heat treatment. High-temperature decomposition of metal nitrate and glycine effectively yields foam-like materials (Yang et al., 2022). The chemical reactions occurring in this process can be expressed by the following equation:

$$M(NO_3)_x + CH_2NH_2COOH + \frac{35-18x}{12}O_2 \rightarrow \frac{1}{3}M_3O_4 + 2CO_2 + \frac{5}{2}H_2O + \frac{x+1}{2}N_2$$

As seen in Figure 2, it can be said that changing heat treatment temperatures has some effect on the porosity. The samples subjected to lower heat treatment temperatures exhibit relatively wider pore sizes. Clearly, this method enables the synthesis of HEO-based materials at low temperatures, tailored to the desired pore structure. In addition, upon revisiting the above equation, it becomes evident that this desired pore quantity can be attained

through careful control of various fuel (glycine) - oxidizer (metal nitrates) ratios. Similar investigations can be found in existing literature (Amirkhanyan et al., 2020; Shin et al., 2023). Nonetheless, adjusting the fuel quantity, whether increased or decreased, may lead to non-stoichiometry and the presence of residual carbon in the desired structure. Thus, these factors should be carefully considered in the synthesis of new porous materials.

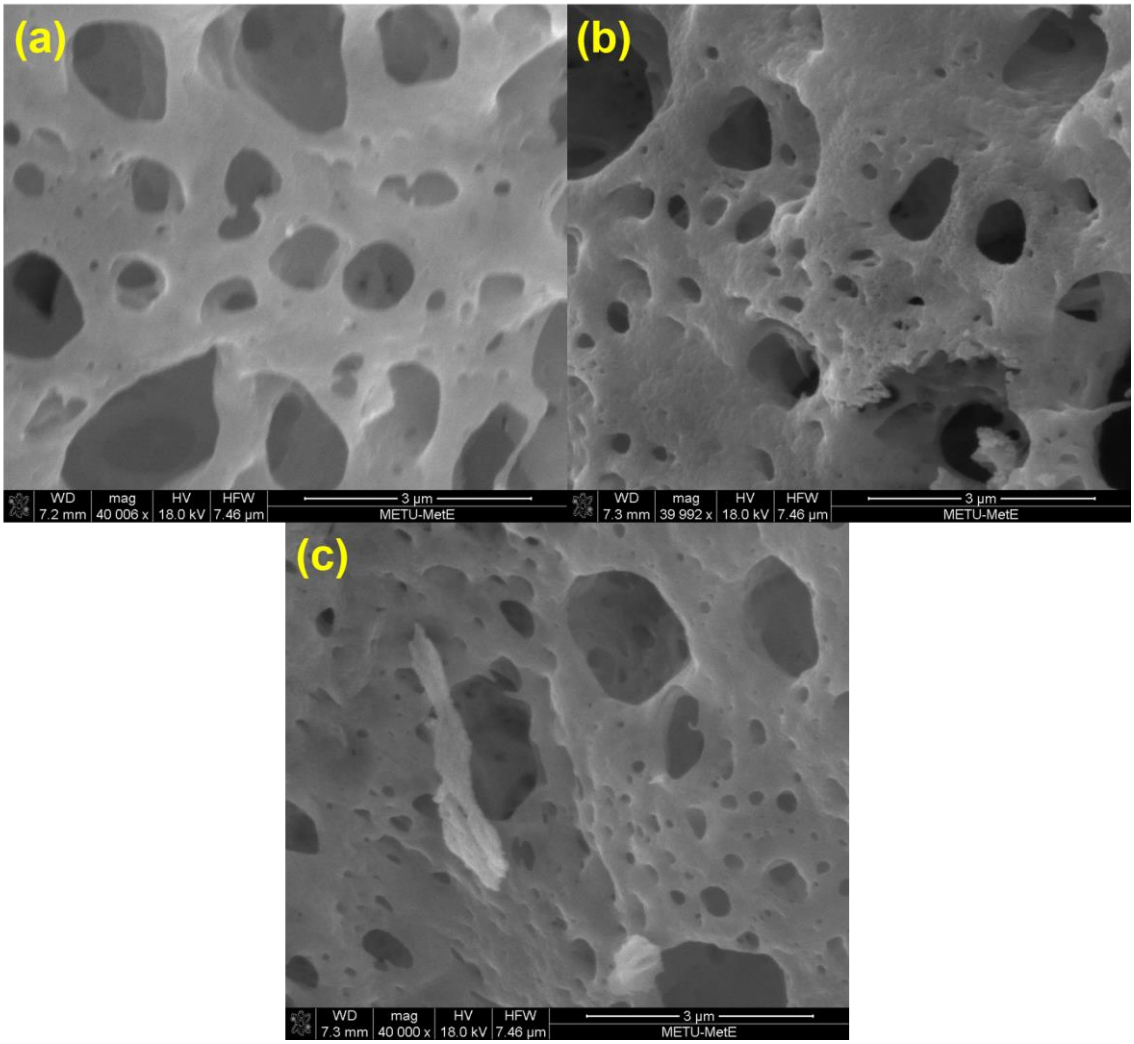

Figure 2. SEM images of the synthesized porous HEO samples at (a) 500 °C (b) 600 °C (c) 700 °C temperatures.

Conclusion

This research focused on creating porous $(FeMnCrCoZn)_3O_4$ high-entropy oxides. The synthesis process involved using glycine as a pore-forming agent through a soft chemistry method at various synthesis temperatures 500 °C, 600 °C and 700 °C. The structural and morphological analysis revealed that the samples were successfully produced with a porous microsheet structure and displayed a single-phase composition in the spinel crystal structure. The synthesis temperature was found to impact the sizes of the pores, as observed. This straightforward and easily scalable synthesis approach for HEO-based materials can also yield porous materials that cannot be prepared by conventional production methods.

Scientific Ethics Declaration

The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

Acknowledgments or Notes

* This article was presented as an oral presentation at the International Conference on Technology, Engineering and Science (www.icontes.net) held in Antalya/Turkey on November 16-19, 2023.

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To cite this article:

Ozden R.C. & Anik, M. (2023) Glycine-assisted synthesis of high surface area $(FeMnCrCoZn)_3O_4$ microsheets. *The Eurasia Proceedings of Science, Technology, Engineering & Mathematics (EPSTEM), 26,* 416-419.