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STEM-EELS Analysis of High Entropy Oxide Nanoparticles

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High entropy oxide (HEO) nanomaterials are new category of ceramic nanomaterials that have promising applications in the field of energy storage, catalysis and biomedical fields attributing to their unique physicochemical properties.[1-3] Five or more immiscible elements can be integrated within a single nanoparticle with high entropy configuration by utilizing synthesis processes with rapid heating and cooling rates.[1, 4] Studies show that the thermodynamic properties, mainly enthalpy and free energy, influence the chemical oxidation states and phase stability of the individual elemental oxide comprised within a HEO configuration.[5] Although substrate dependent or aerosol synthesis methods are utilized for the successful synthesis of near equimolar high entropy oxide nanomaterials, there exists a knowledge gap in the fundamental understanding of transition of oxidation states from unary metal oxides to binary, ternary, quaternary and quinary HEOs. The investigation of oxidation states and chemical shifts of individual elements during their alloying composition evolution can reveal novel atomistic attributes of elemental affinities towards each other and of their corresponding crystal phase evolution to achieve the final stable structure within an entropy configuration.

In the present work, the HEO nanoparticles composed of Mn, Fe, Ni, Cu, Zn elements are synthesized by flame spray pyrolysis method. **Figure 1** indicates the atomic resolution spinel crystal structure of high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) image of synthesized HEO nanoparticle. **Figure 2** shows the electron energy loss spectroscopy (EELS) elemental mapping and high energy loss spectrum acquired from a single quinary HEO nanoparticle. To investigate the crystal phase and oxidation state evolution unary – Fe oxide and Mn oxide, binary – Mn/Fe oxide, ternary – Mn/Fe/Ni oxide, quaternary – Mn/Fe/Ni/Cu oxide and quinary – Mn/Fe/Ni/Cu/Zn oxide nanoparticles are produced under the same synthesis conditions. Results indicate that the high-resolution EELS analysis of $L_{3,2}$ edges of individual elements in the high loss and M-edges in the low-loss regions, and corresponding energy loss near edge spectroscopy (ELNES) features enable the identification of oxidation states and chemical shifts for each element within a quinary HEO configuration, which also can predict tetragonal and octagonal occupancy of selective cations in the complex spinel crystal structure. The EELS results also show that the oxidation states for the each of five elements varies considering their respective coordination with oxygen element and possibly with the neighboring metal cations. To investigate the chemical affinity towards each other and the role of each metal cations as an electron-acceptor and electron-doner within a HEO configuration, additionally the systematic EELS analysis of unary, binary, ternary and quaternary entropy oxide nanoparticles is performed. Conclusively, fundamental oxidation state evolution for Fe and Mn elements from unary to quinary high entropy oxide configurations helps in understanding the chemical affinity and coordination among metal cations to achieve the final high entropy stable crystal structure. These results will provide the key insights for tailoring the properties of complex HEO nanomaterials according to the specific industrial applications.

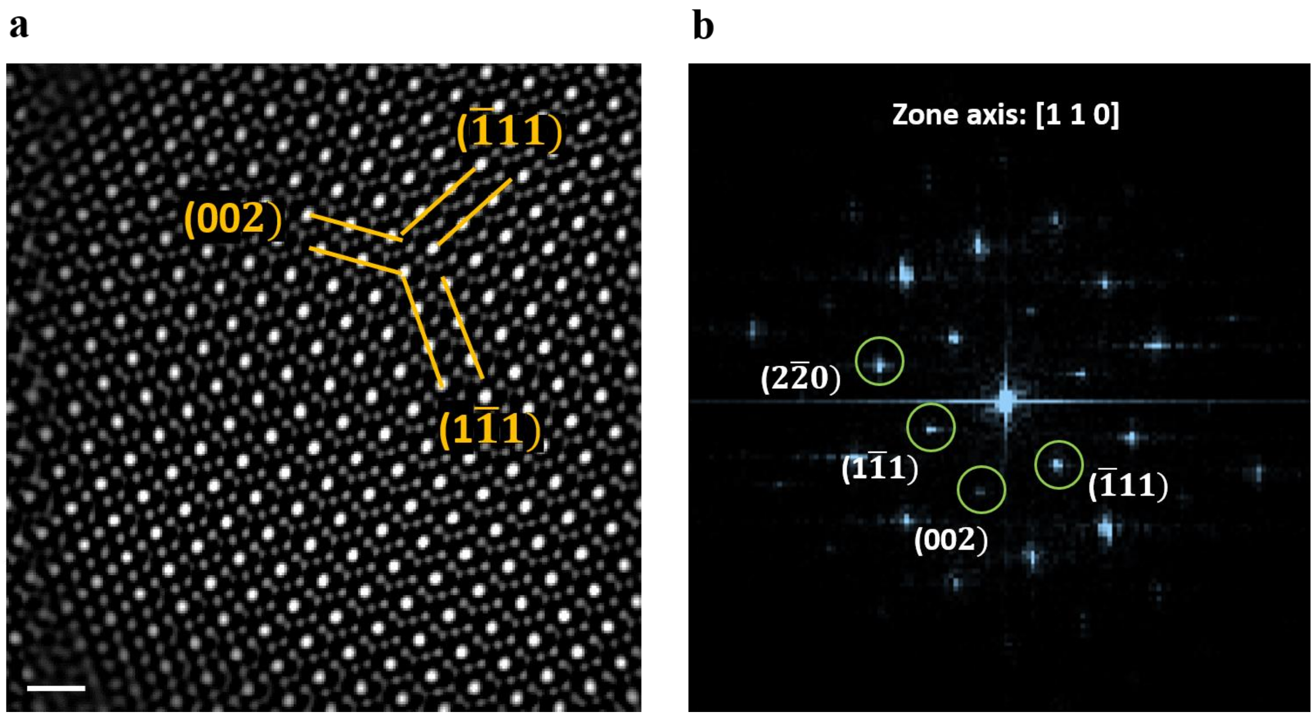

Figure 1. Figure 1. Crystal structure analysis of high entropy oxide nanoparticle. (a) Atomic resolution IFFT HAADF-STEM image indicating the crystal planes and revealing the spinel crystal structure (Scale bar represents 1 nm). (b) FFT analysis of high entropy oxide nanoparticle indicating lattice planes in the reciprocal space.

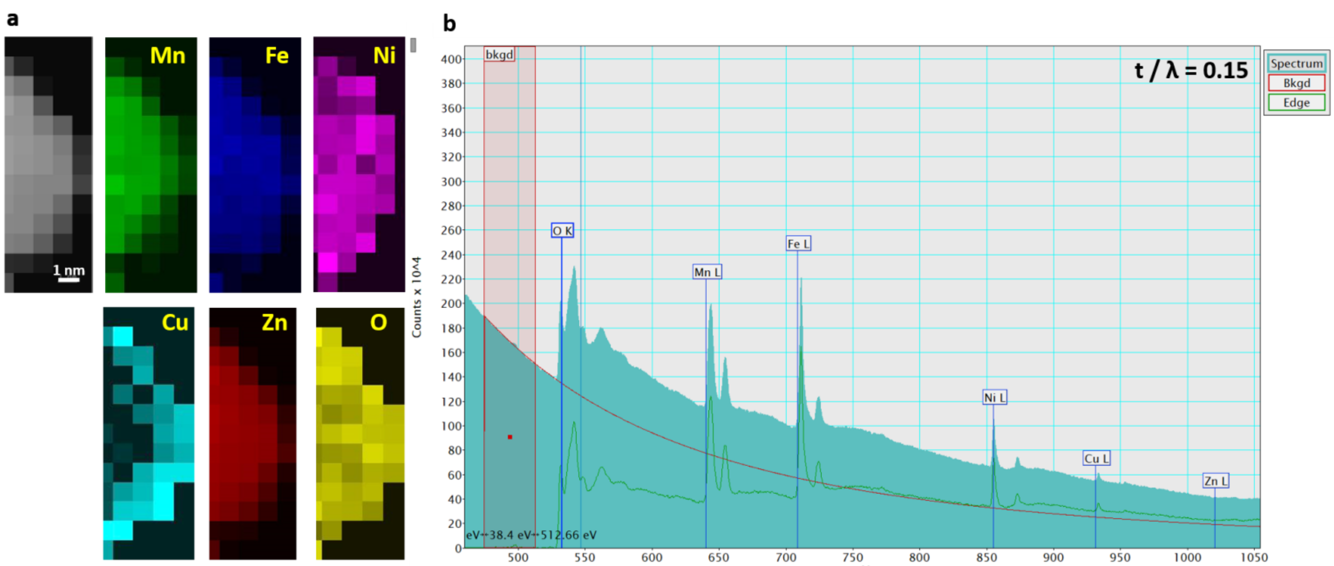

Figure 2. Figure 2. STEM-EELS elemental mapping and high loss spectrum of high entropy oxide nanoparticle region acquired with 0.3 eV/ch dispersion confirming the presence of all five (Mn, Fe, Ni, Cu, Zn) metal oxides.

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