INVESTIGATING THE INFLUENCE OF Pr CONCENTRATION ON THE STRUCTURAL EVOLUTION OF CERIA-BASED HIGH-ENTROPY OXIDES

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Introduction

High-entropy oxides (HEOs) are a class of multifunctional materials consisting of five or more cations incorporated into a single crystal lattice. Their high configurational entropy stabilizes complex solid solutions and promotes the formation of unique defect structures, making them promising candidates for photocatalytic and environmental remediation applications. Among these materials, ceria-based HEOs have attracted significant interest owing to the reversible Ce^{4+}/Ce^{3+} redox couple and their high capacity for oxygen vacancy formation. In this study, the effect of Pr incorporation on the structural evolution, defect chemistry, and photocatalytic degradation of methylene blue was systematically investigated.

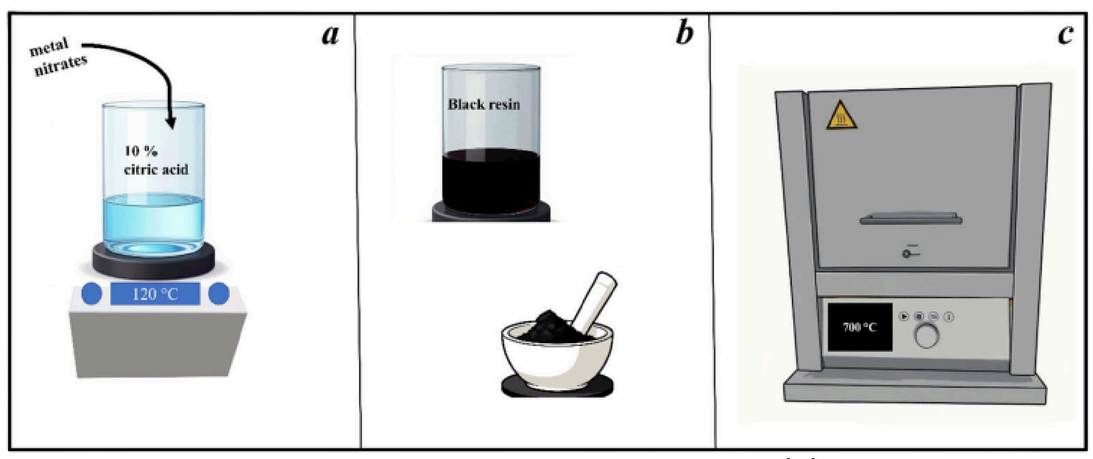

Figure 1. Overview of the synthesis process showing: (a) preparation of a metal nitrate–citric acid solution followed by heating at 120 °C, (b) formation and grinding of the resulting black resin, and (c) calcination at 700 °C to obtain the high-entropy oxide powders.

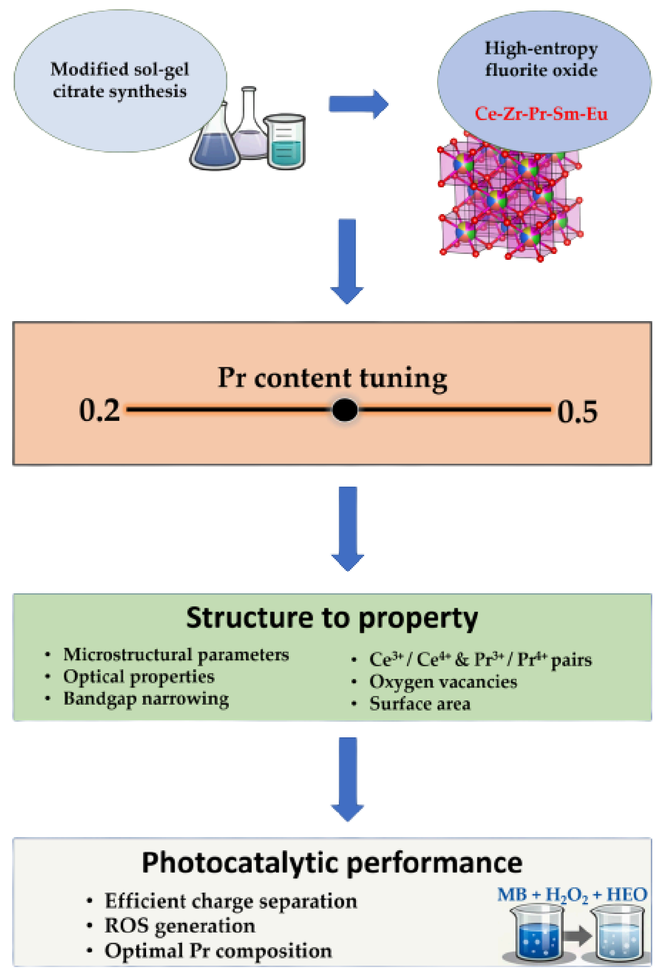

Figure 2. Schematic overview of the experimental workflow.

Results

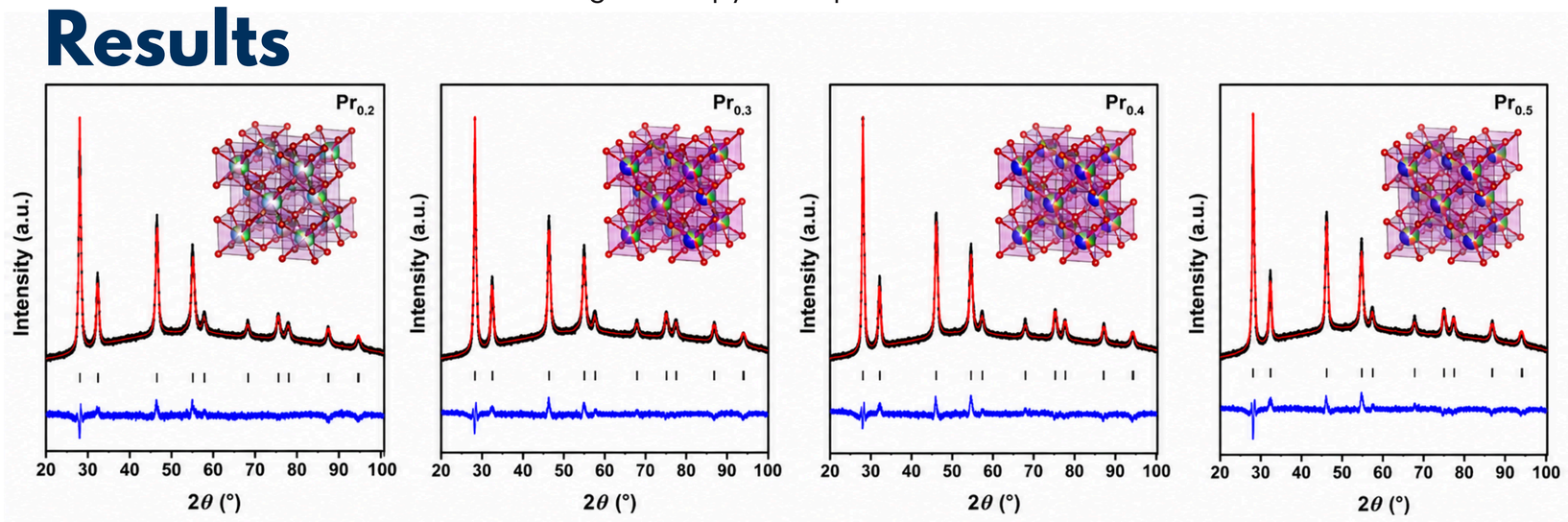

Figure 3. Rietveld refinement patterns of the synthesized high-entropy oxides, with the corresponding crystal structure models displayed in the insets. The experimental X-ray diffraction patterns are shown as black curves, the calculated profiles as red curves, the Bragg reflection positions as black tick marks, and the difference between the experimental and calculated patterns as blue curves. In the crystal structure models, oxygen atoms are shown in red, while the individual cation species are distinguished by different colors, with praseodymium specifically highlighted in blue.

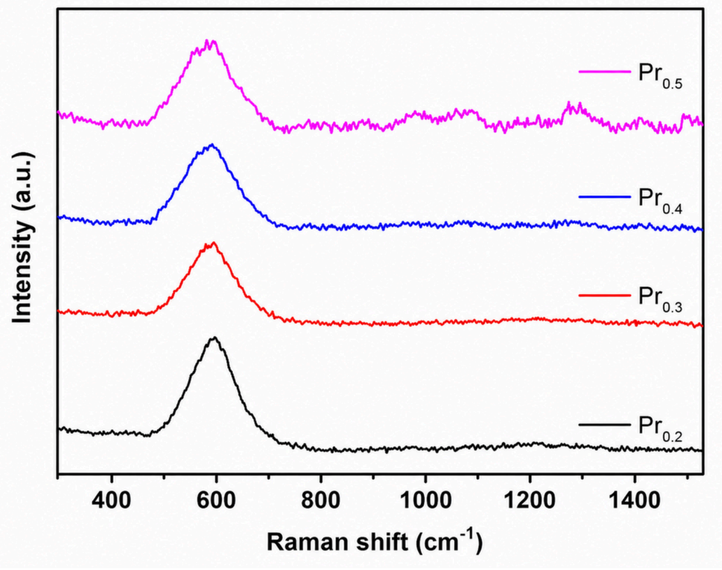

Figure 4. Raman spectra of synthesized compounds

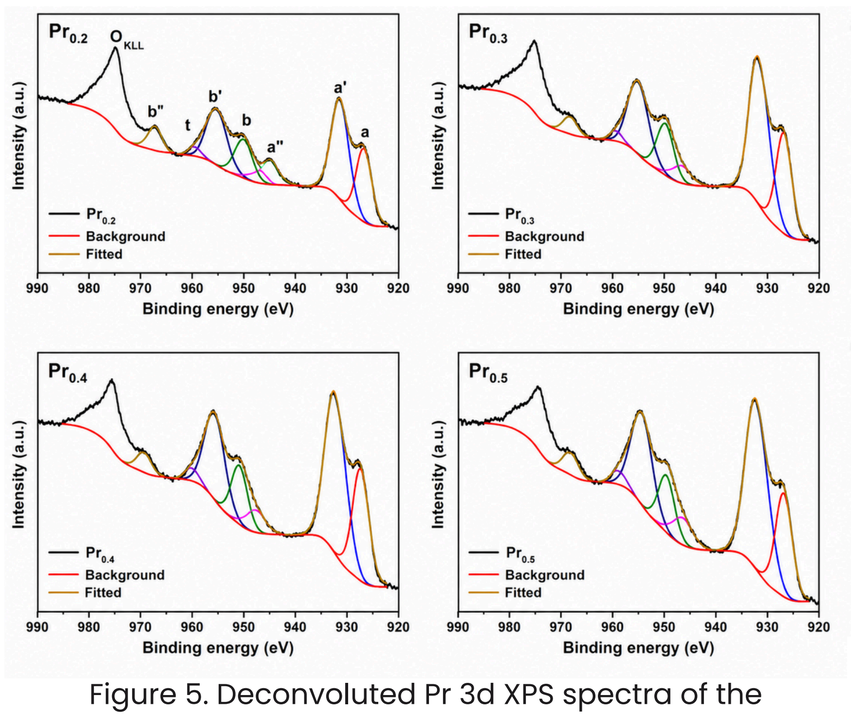

Figure 5. Deconvoluted Pr 3d XPS spectra of the synthesized high-entropy oxides. Quantitative analysis revealed a gradual decrease in the relative surface Pr^{3+} fraction from 47.9% ($Pr_{0.2}$) to 36.1% ($Pr_{0.5}$), indicating progressive oxidation and enhanced stabilization of Pr species with increasing Pr^{4+} incorporation.

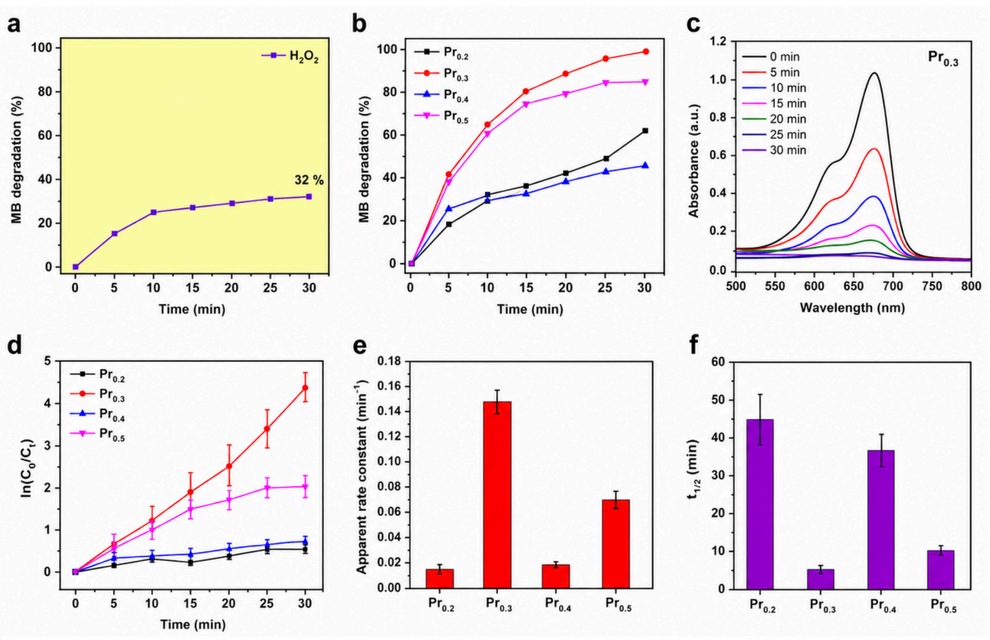

Figure 6. Photocatalytic degradation of methylene blue (MB) using H_2O_2 alone (a) and in the presence of synthesized high-entropy oxide photocatalysts (b). UV–Vis absorption spectra recorded during MB degradation over the $Pr_{0.3}$ catalyst within a 30 min irradiation period (c). Pseudo-first-order kinetic plots expressed as $ln(C_0/C_t)$ versus irradiation time (d), corresponding apparent rate constants (e), and calculated half-life times ($t_{1/2}$) for all investigated photocatalysts (f).

Conclusions

- Single-phase high-entropy fluorite oxides were successfully synthesized.
- Increasing Pr incorporation induced lattice expansion and enhanced defect formation.
- Mixed-valence Ce and Pr species promoted oxygen vacancy generation and bandgap narrowing.
- Moderate Pr content enhanced charge separation and improved redox performance.
- The $Pr_{0.3}$ composition achieved 98.9% methylene blue degradation within 30 min.
- High-entropy defect engineering provides an effective strategy for advanced photocatalytic wastewater treatment.