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A High-Entropy Zirconate Pyrochlore for Multifunctional Photocatalysis

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INTRODUCTION & AIM

- **Industrial wastewater** containing persistent **dyes** and toxic **heavy metals** like Cr(VI) poses a severe **environmental threat**.
- These contaminants pose serious **risks** to **human health**, including **cancer** and **organ damage**, and adversely **affect aquatic ecosystems**.
- **Photocatalysis** offers a **sustainable solution**, but materials often lack versatility or stability.
- **Pyrochlore oxides** ($A_2B_2O_7$) offer **structural flexibility**, high oxygen mobility, and **tunable electronic properties**, making them attractive for photocatalytic applications.
- **High-entropy materials**, which contain **five or more principal elements** in near-equimolar ratios, stabilize single-phase solid solutions and allow **synergistic interactions** among multiple cations.
- **Aim:** To design, synthesize, and evaluate a novel high-entropy pyrochlore oxide as a single-phase, stable, and multifunctional photocatalyst for the degradation of diverse pollutants.
- **Core Innovation:** Utilizing the high-entropy concept—mixing five principal cations (Ce, Pr, Zn, Nd, Tb) in equal ratios—to create a stabilized crystal structure with tunable electronic properties and enhanced functionality.

METHOD

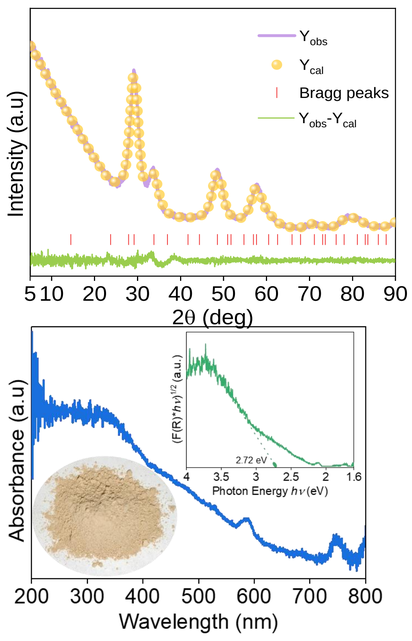
- **Synthesis:** $(Ce_{0.2}Pr_{0.2}Zn_{0.2}Nd_{0.2}Tb_{0.2})_2Zr_2O_7$ nanoparticles were synthesized **via a modified Pechini** (sol-gel) method.
- **Stoichiometric amounts** of cerium(III) nitrate, praseodymium(III) nitrate, zinc nitrate, neodymium(III) nitrate, terbium(III) nitrate, and zirconium(IV) oxynitrate were dissolved in deionized water.
- **Citric acid** and **ethylene glycol** were added as **chelating and polymerizing agents**, and the mixture was heated at 110 °C to form a viscous gel.
- The **gel** was dried at **300 °C for 2 h** and then **calcined** at **500 °C for 4 h** to remove organics and crystallize the oxide.
- **Characterization:**
- **XRD:** Phase purity and crystal structure.
- **FESEM:** Morphology and particle size.
- **XPS/UPS:** Elemental states and band structure.
- **UV-Vis Spectroscopy:** Optical properties.

Photocatalytic Tests: UV light (365 nm) against:
1.Cationic dye: Methylene Blue (MB, 50 ppm)
2.Anionic dye: Congo Red (CR, 50 ppm)
3.Heavy metal: (Cr(VI), 50 ppm)

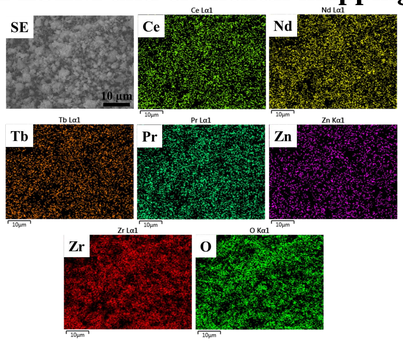
RESULTS & DISCUSSION

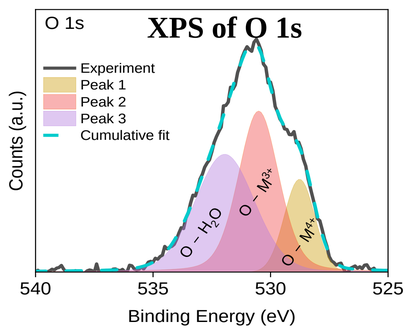
- **XRD** analysis confirmed a **single-phase cubic pyrochlore structure** (space group Fd-3m) with a lattice parameter of **10.594 Å from Rietveld refinement**.
- The **ratio of average A-site cation radii to B-site** cation radius was **1.477**, well within the **1.46–1.78 range** required for a **stable pyrochlore structure**.
- **No secondary phases were detected**, indicating successful incorporation of all five principal elements into the pyrochlore lattice.
- FESEM images revealed highly agglomerated nanoparticles with irregular shapes, typical of high-surface-energy particles undergoing coalescence during calcination.
- **EDS elemental mapping showed uniform spatial distribution** of Ce, Pr, Zn, Nd, Tb, Zr, and O, and quantitative analysis confirmed near-stoichiometric compositions.

XRD pattern with Rietveld plot



FESEM and elemental mapping

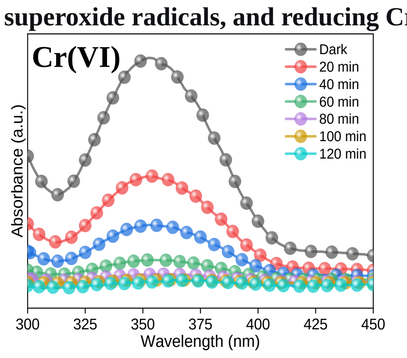


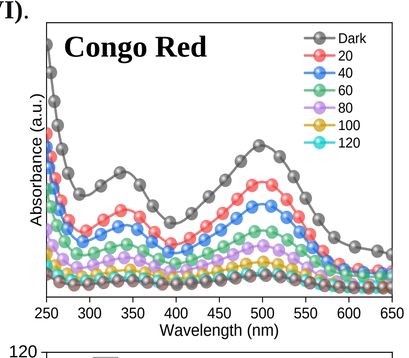


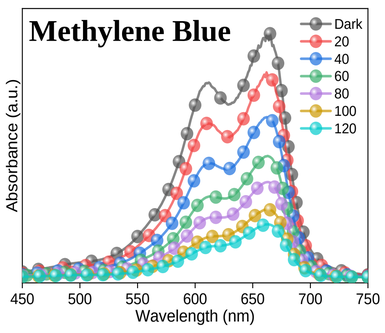
UV Visible and Bandgap estimation

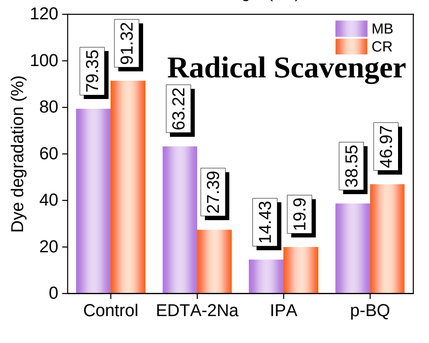
- **UV-visible spectroscopy** displayed a strong absorption band in the UV region (< 400 nm), attributed to charge transfer from oxygen 2p to metal 3d/4f orbitals.
- The **Kubelka-Munk plot** yielded an optical bandgap of **2.72 eV**, narrower than many pristine pyrochlores due to **oxygen vacancies and mixed valence states of Ce and Pr**.

- **UPS analysis** determined the work function and valence band edge relative to vacuum; combined with the optical bandgap, the conduction band edge was calculated.
- With respect to the normal hydrogen electrode (NHE), the valence band maximum is **+0.63 V** and the conduction band minimum is **–2.09 V**, which are thermodynamically favorable for **generating hydroxyl radicals, superoxide radicals, and reducing Cr(VI)**.









- **Reaction kinetics** followed a **pseudo-first-order model**; rate constants (k) were derived from **ln(C_0/C)** versus time plots.
- **Cr(VI) reduction:** k = 0.0506 min^{-1}, achieving 98.8% removal after 120 min.
- **Congo red degradation:** k = 0.0183 min^{-1}, achieving 91.3% degradation after 120 min.
- **Methylene blue degradation:** k = 0.0128 min^{-1}, achieving 79.3% degradation after 120 min.
- **Radical trapping experiments** were conducted using isopropyl alcohol (IPA) for hydroxyl radicals (•OH), p-benzoquinone (p-BQ) for superoxide radicals (O_2•$^-$), and EDTA-2Na for holes (h^+).
- The addition of each scavenger significantly reduced degradation efficiency, indicating that all **three species contribute to the photocatalytic process**.
- This novel high-entropy oxide performs better than or comparably to many recently reported complex heterojunction photocatalysts, highlighting the power of the high-entropy design.
- The photocatalyst **was successfully recycled for three consecutive cycles** with only a slight decrease in performance (**likely due to material loss during recovery**).

CONCLUSIONS

- A novel single-phase high-entropy zirconate pyrochlore, $(Ce_{0.2}Pr_{0.2}Zn_{0.2}Nd_{0.2}Tb_{0.2})_2Zr_2O_7$, was successfully synthesized using a simple modified Pechini method.
- The material exhibits a cubic pyrochlore structure, a crystallite size of 4.5 nm, a bandgap of 2.72 eV, and a high concentration (39.8%) of oxygen vacancies.
- Excellent photocatalytic activity for Cr(VI) reduction (k = 0.0506 min^{-1}) and degradation of Congo red (k = 0.0183 min^{-1}) and methylene blue (k = 0.0128 min^{-1}) under UV light.
- The photocatalyst retains its single-phase structure and good activity over three reuse cycles, highlighting its potential for practical wastewater treatment.

FUTURE WORK/ REFERENCES/ACKNOWLEDGMENT

- Future directions include compositional tuning to achieve visible-light absorption, enabling efficient use of solar energy.
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