Band gap Engineering in Novel Fluorite-Type Rare Earth High-Entropy Oxides (RE-HEOs) with Computational and Experimental Validation for Photocatalytic Water Splitting Applications

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INTRODUCTION

Five different rare-earth-based nanocrystalline high entropy oxides (HEOs) with fluorite type of structure and average crystallite sizes between 6 and 8 nm were prepared and their photocatalytic behavior towards AZO dye degradation and photoelectrochemical water splitting for hydrogen generation was examined. The cationic site in the fluorite lattice consists of five equimolar elements selected from the group of rare-earth elements including La, Ce, Pr, Eu, and Gd and second-row transition metals, Y and Zr. Studied HEOs exhibit bandgaps in the range from 1.91 eV to 3.0 eV and appropriate valence and conduction bands for water splitting. They reveal high photocatalytic activity that is mostly attributed to the accessibility of more photocatalytic active sites which provided radicals responsible for the AZO dye degradation. The materials successfully produce hydrogen by photocatalytic water splitting, suggesting the potential of HEOs as new photocatalysts. The photocatalytic performances of all studied HEOs outperform the single fluorite oxides or equivalent mixed oxides. The $Ce_{0.2}Zr_{0.2}La_{0.2}Pr_{0.2}Y_{0.2}O_2$ (CZLPY) engender hydrogen in 9.2 µmolmg⁻¹ per hour that is much higher content than for pristine CeO₂ material which amounts to 0.8 µmolmg⁻¹ per hour. The explanation of the obtained experimental results is supported by density functional theory (DFT) calculations. The density of states (DOS) and the projected DOS after high-entropy equimolar doping (CZLPY) of starting pristine CeO₂ indicated that the bandgap is significantly reduced from 3.48 to 2.71 eV due to Pr 4f and 0 2p orbital mixing. DFT calculation also disclose that a strong interaction between AZO dye methylene blue (MB) and CZLPY(111) is responsible for observed higher photodegradation of MB by CZLPY compared to pristine CeO₂. This occurs due to the existence of three solid bondings of MB with the surface of CZLPY(111) compared to only one solid bonding with the surface of CeO_2 (111).

STRUCTURAL CHARACTERIZATION AND CATALYTIC ACTIVITY



Figure 1. Rietveld plots of the investigated synthesized HEO catalysts with visualized fluorite-type crystal structure in the insets.





Figure 3. PEC performance of HEOs showing LSV plots under chopped dark and solar-light

Figure 2. Survey XPS spectrum of CZLPY (a) and high resolution deconvoluted spectra of: (b) cerium, (c) zirconium, (d) lanthanum, (e) praseodymium, (f) yttrium, (g) oxygen and (h) carbon.

Table 1. Saturated photocurrent density and HER activity trend w.r.t. structural properties of the catalysts.

condition. (a) Potential vs. Ag/AgCl (V) and (b) Potential vs. RHE (V); (c) Photo switching transient behaviour of CZLPY electrode; (d) LSV plots of CZLPY electrode with varied coating thickness (1,2,3) under chopped light and dark conditions; (e) Applied bias photon-to-current efficiency (ABPE, η %) vs potential in RHE scale plot for CZLPY electrode; (f) Electrochemical impedance spectroscopy data obtained for CZLPY electrode under dark and light condition; (g) Time-dependent hydrogen (H₂) evolution by pure CeO₂ and HEOs under solar irradiation and their (h) corresponding hydrogen production rate after 2 hours of constant irradiation; (i) Stability test showing catalytic activity of CZLPY catalyst over four sequential cycles.

Catalyst	Surface [O _V +O _H]/ [O _V +O _H +O _L] (%)	HER activity in 2 hrs (µmolmg ⁻¹)	Surface [Pr ³⁺]/ [Pr ³⁺ + Pr ⁴⁺] (%)	Surface [Ce ³⁺]/ [Ce ³⁺ + Ce ⁴⁺] (%)	D _{av} (nm)	ε _{av} (×10 ⁻⁴)	S _{BET} (m ² g ⁻¹)	Saturated Photocurrent Density (j) (µAcm ⁻²)
CLPEY	24.8	5	76.3	11.9	6	57.50	23.4	17
CZLGY	26.2	8.5	0	14.9	6	38.60	61.4	21
CLPEG	26.6	9.2	77.3	20.4	8	51.73	30.8	22
CLPGY	29.1	14	76.3	22.2	7	58.40	23.4	25
CZLPY	40.4	18.4	84.7	19.3	6	25.20	24.3	35

DFT: COMPUTATIONAL METHODOLOGY







CONCLUSIONS

In summary, we have successfully synthesized five different rare-earth-based high-entropy oxides in nanocrystalline form via a modified aqueous sol-gel route. All examined HEOs represent equimolar 5-cation system selected from the elements: Ce, Zr, La, Pr, Gd, Eu, Y that were uniformly distributed and demonstrated a single fluorite structure with lattice parameter similar as parent simple oxide CeO₂. The variation of equimolar chemical composition yielded the band gap variation and modulation of electronic structure. Among studied HEOs, Ce_{0.2}Zr_{0.2}La_{0.2}Pr_{0.2}V_{0.2}O₂ (CZLPY) has shown the highest photocatalytic activity in AZO dyes degradation and photocatalytic water splitting in hydrogen generation than any other synthesized HEOs due to the presence of optimum level of Pr³⁺, Ce³⁺ and the highest content of oxygen vacancies as verified by XPS. Thus, the phase stabilization of high-entropy oxide in parent CeO₂ lattice induced more lattice distortion, more Ce³⁺ concentration, more oxygen vacancies and additional energy levels (due to more oxidation states of Ce and Pr) as compared to pure CeO₂. According to the DFT calculations, the most appropriate model of the crystal structure of CZLPY is the one where O anions are tetrahedrally coordinated with four different (Ce, La, Zr, Pr, Y) cations. The most stable fluorite surface along [111] is verified as a model/catalyst for Zr, La, Pr, and Y dopants, followed by the interaction with water and MB molecules. Based on experimental findings and theoretical modelling, this work provides a significant step for enhancing the photocatalytic performance of rare-earth-based HEOs.