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 CeO_2 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 CeO_2 indicated that the bandgap is significantly reduced from 3.48 to 2.71 eV due to Pr 4f and O 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 CeO_2. 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

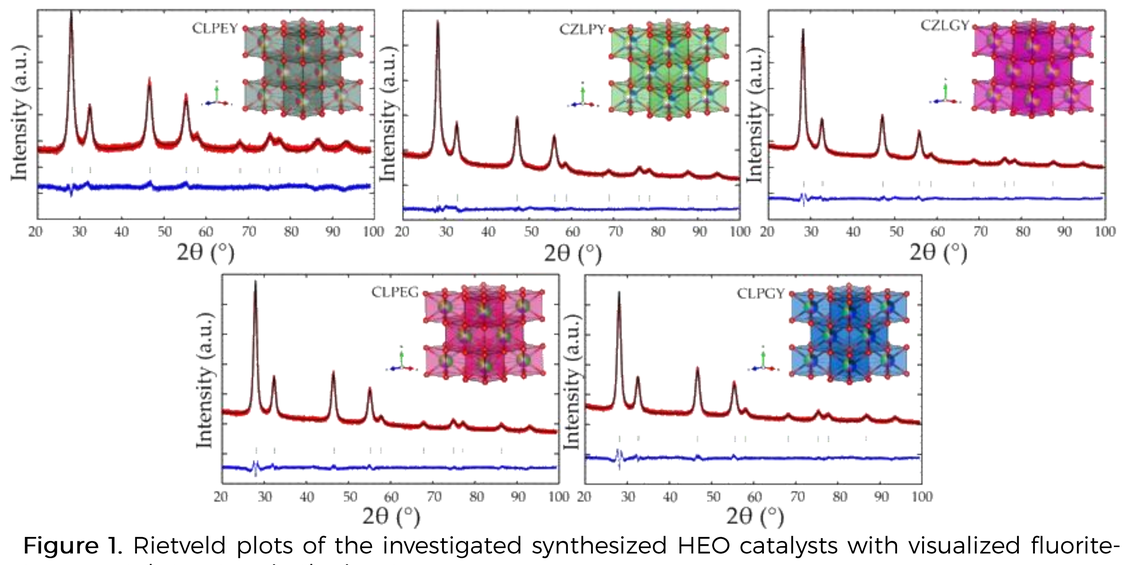

Figure 1. Rietveld plots of the investigated synthesized HEO catalysts with visualized fluorite-type crystal structure in the insets.

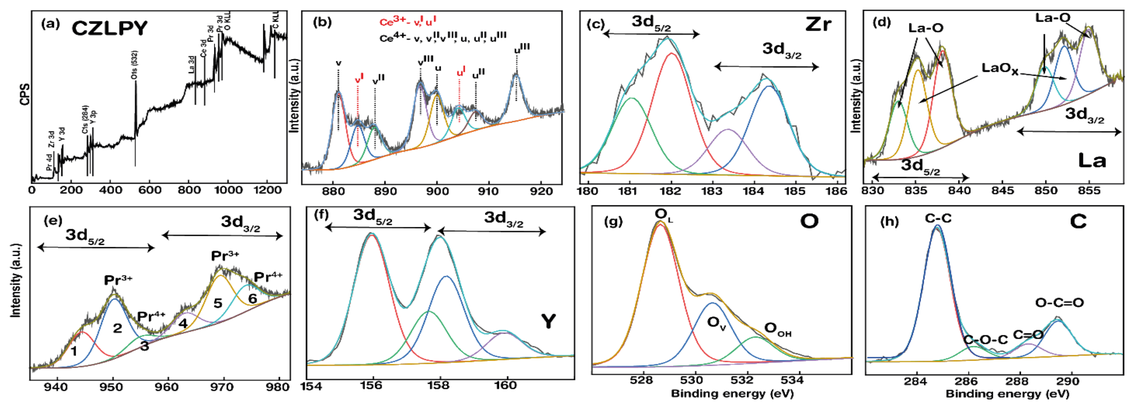

Figure 2. Survey XPS spectrum of CZLPY (a) and high resolution deconvoluted spectra of: (b) cerium, (c) zirconium, (d) lanthanum, (e) praseodymium, (f) yttrium, (g) oxygen and (h) carbon.

Catalytic activity

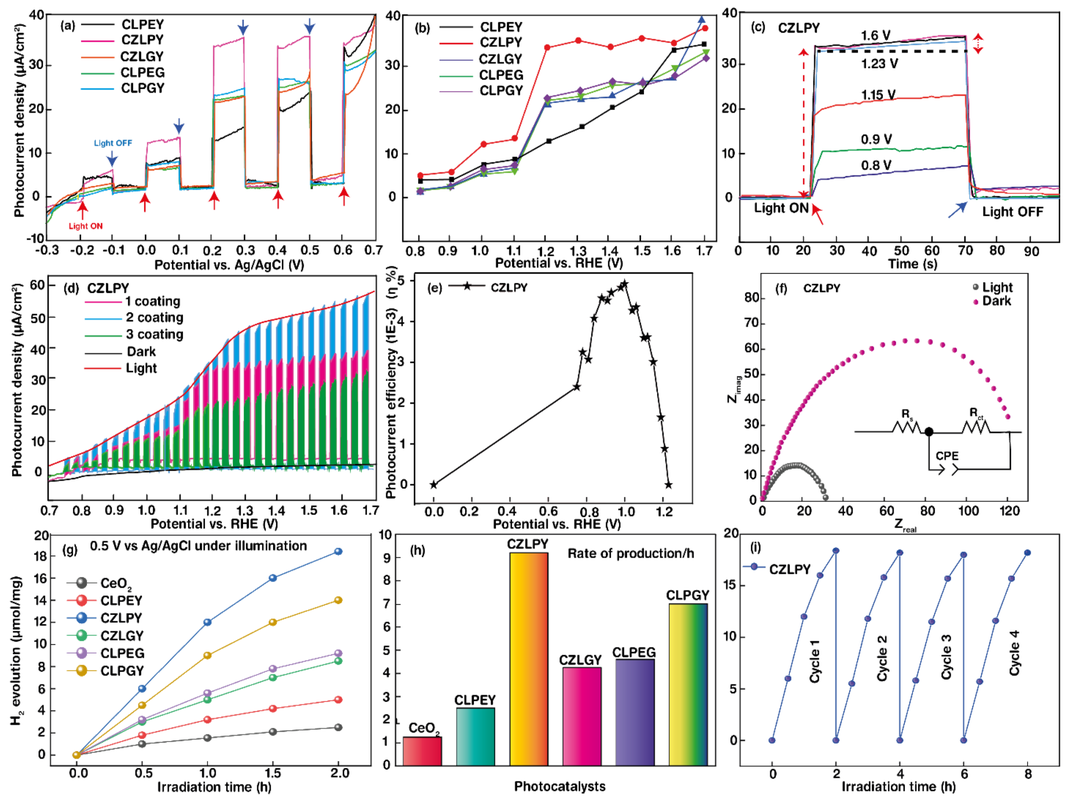

Figure 3. PEC performance of HEOs showing LSV plots under chopped dark and solar-light condition. (a) Potential vs. Ag/AgCl (V) and (b) Potential vs. RHE (V); (c) Photo switching transient behaviour of CZLPY electrode; (d) LSV plots of CZLPY electrode with varied coating thickness (1,2,3) under chopped 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 CeO_2 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.

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

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} ($\times10^{-4}$)	S_{BET} (m^2g^{-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

Table 4. DFT calculated ground state relative energy of pristine 1x5x5 supercell of CeO_2 along with three possible proposed models

Species	Relative energy [eV]	Band gap [eV]
Pristine CeO_2	38641.65	3.48
Model 1	44569.27	0.93
Model 2	44571.35	0.65
Model 3	44573.94	2.71

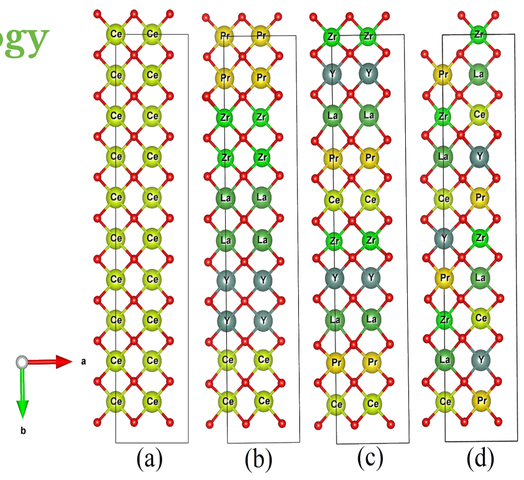

Figure 4. 1x5x1 supercell of CeO_2 (a), along with (b-d) three possible models of Y, Pr, Zr, and La-doped 1x5x1 CeO_2 (CZLPY).

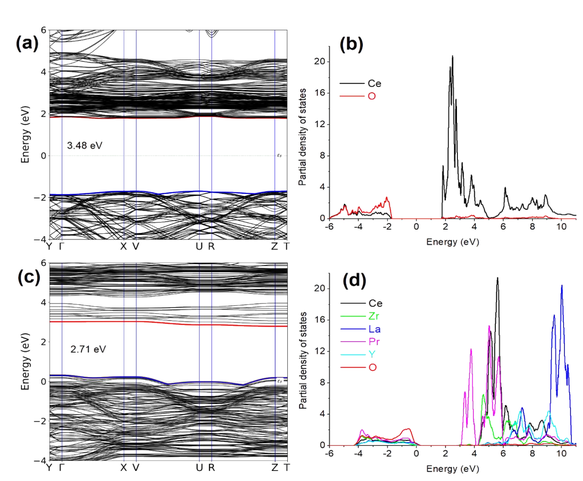

Figure 5. (a-b) Band structure along with PDOS plot of pristine 1x5x1 CeO_2; (c-d) and Model 3. The Fermi energy in all these plots is set to zero.

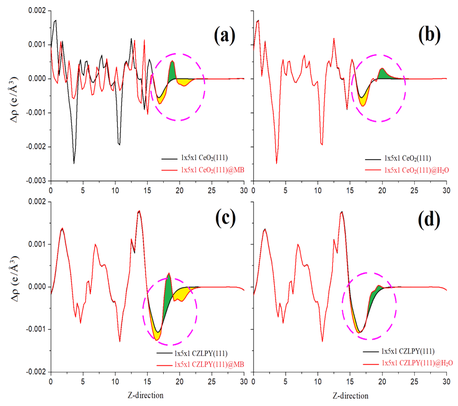

Figure 6. Average electron density difference ($\Delta\rho$) along the Z-direction for pristine ceria and CZLPY (black line) along with pristine water and MB interacted species (red line). The green- and yellow shaded areas indicate electron donation and accumulation, respectively.

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, $Ce_{0.2}Zr_{0.2}La_{0.2}Pr_{0.2}Y_{0.2}O_2$ (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 Pr^{3+}, Ce^{3+} and the highest content of oxygen vacancies as verified by XPS. Thus, the phase stabilization of high-entropy oxide in parent CeO_2 lattice induced more lattice distortion, more Ce^{3+} concentration, more oxygen vacancies and additional energy levels (due to more oxidation states of Ce and Pr) as compared to pure CeO_2. 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.