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

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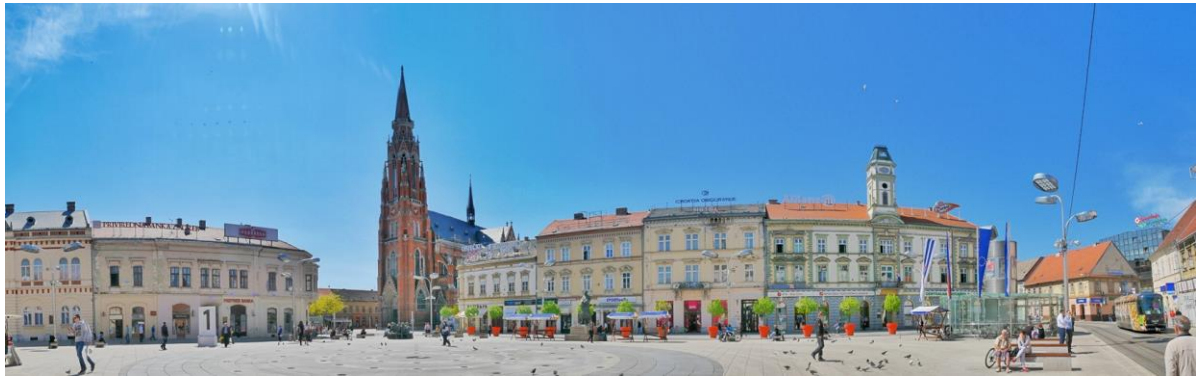
Osijek



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THEORETICAL BACKGROUND

About the idea

Hydrogen

Clean, efficient, the most renewable and sustainable source of energy

Hydrogen fuel

Photoelectrochemical water splitting

H_2

AZO DYES

Azo dyes

Heavy elements (Pb, As, Cr, Cd, Hg)

Cleaning the water and using it for hydrogen generation

HEOs

Ceria (CeO_2)

Effective photocatalyst

Excellent redox potential characteristics

Oxygen vacancies

High entropy oxides (HEOs)

5 or more cations, incorporated within a single-phase system

Charge, ionic radii, coordination number

Enhanced catalytic behaviour

IMPLEMENTATION OF THE IDEA

Synthesis

Five novel single-phase HEOs

Average crystallite sizes ranging from 6-8 nm

Eco-friendly aqueous sol-gel citrate route.

Characterization

Detailed characterization of the as-synthesized HEOs and performance measurements.

DFT

Theoretical calculations to establish a plausible mechanism for photocatalytic detoxification of MB.

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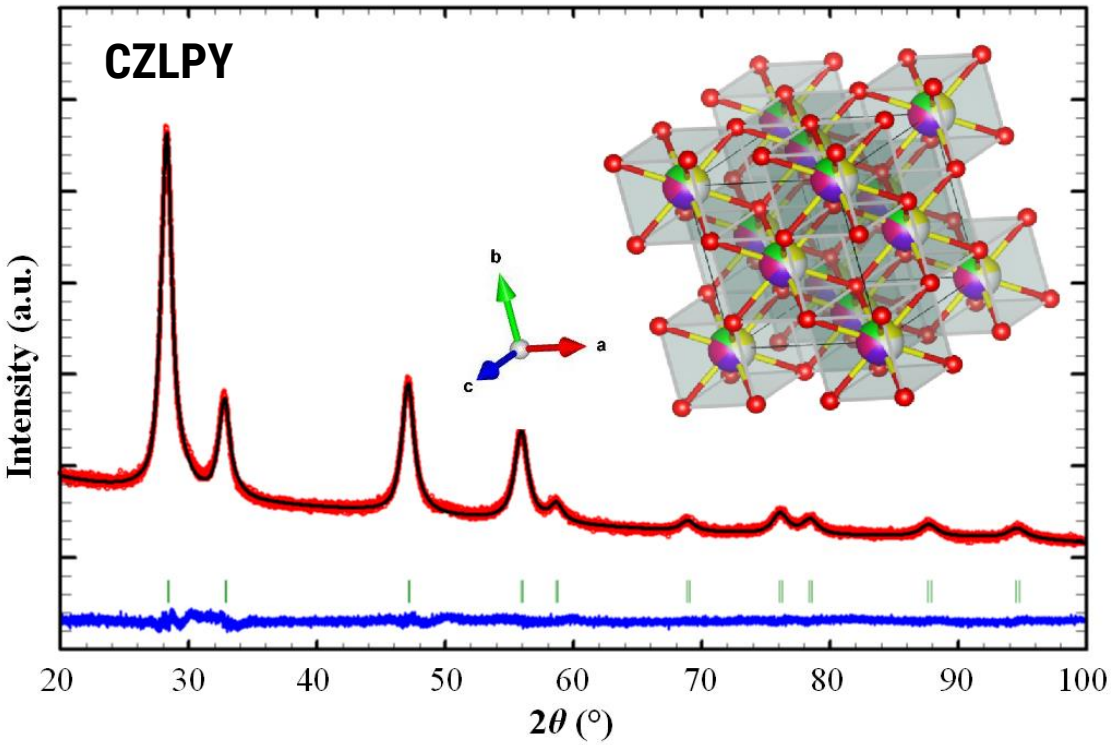
STRUCTURAL CHARACTERIZATION

SYNTHESIZED HEOs

COMPOUNDS	CHEMICAL FORMULA
CLPEY	$Ce_{0.2}La_{0.2}Pr_{0.2}Eu_{0.2}Y_{0.2}O_2$
CZLPY	$\mathbf{Ce_{0.2}Zr_{0.2}La_{0.2}Pr_{0.2}Y_{0.2}O_2}$
CZLGY	$Ce_{0.2}Zr_{0.2}La_{0.2}Gd_{0.2}Y_{0.2}O_2$
CLPEG	$Ce_{0.2}La_{0.2}Pr_{0.2}Eu_{0.2}Gd_{0.2}O_2$
CLPGY	$Ce_{0.2}La_{0.2}Pr_{0.2}Gd_{0.2}Y_{0.2}O_2$
CLPEY	$Ce_{0.2}La_{0.2}Pr_{0.2}Eu_{0.2}Y_{0.2}O_2$

POWDER X-RAY DIFFRACTION

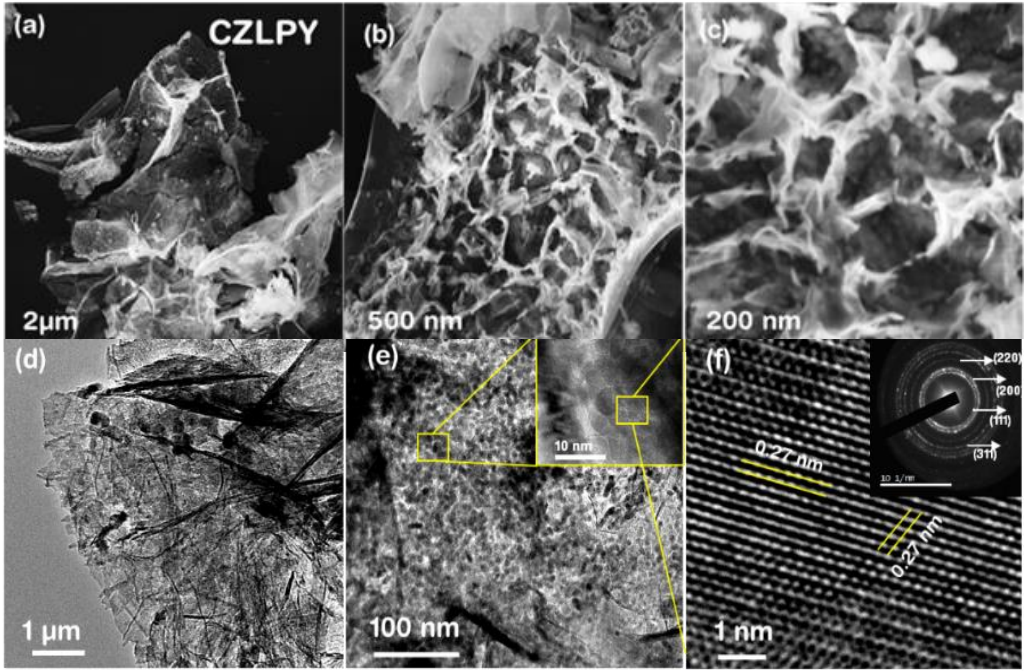


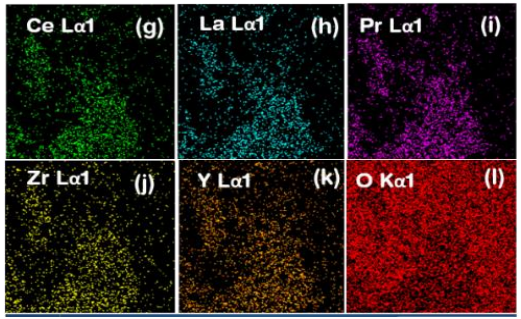
Phase purity, crystal structure and microstructural features

Fm-3*m* space group

CZLPY – highest degree of crystal lattice order

ELECTRON MICROSCOPY



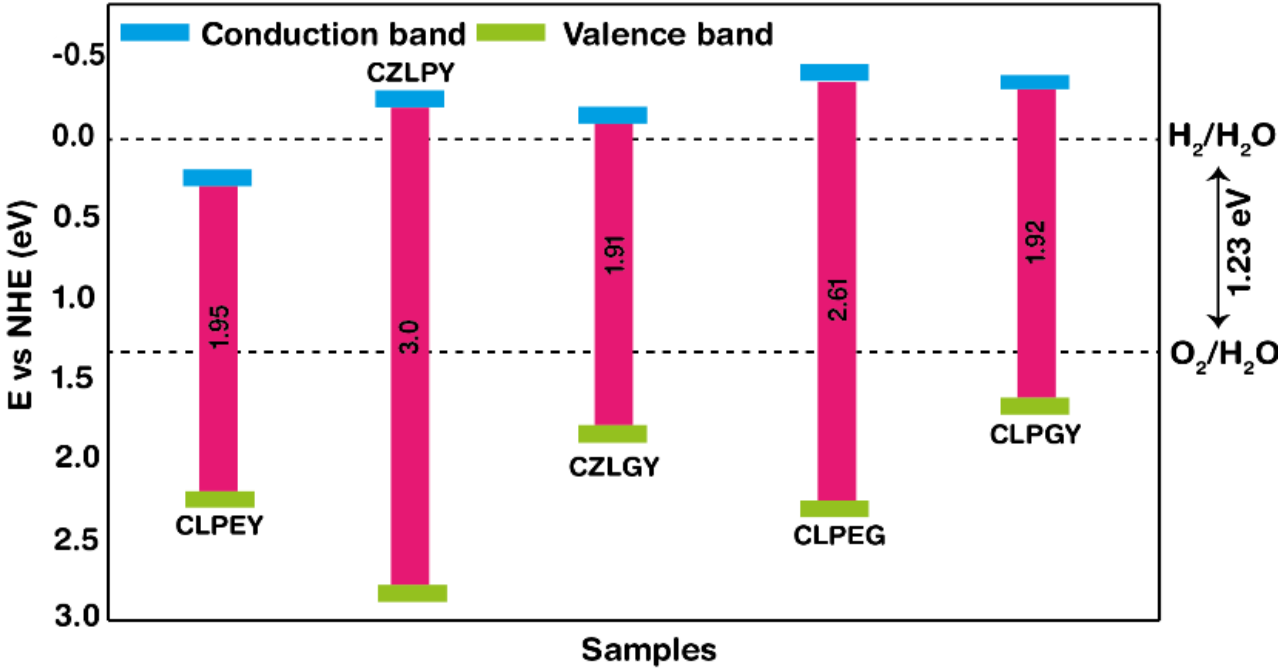


General morphology

Crystallite size and crystallinity

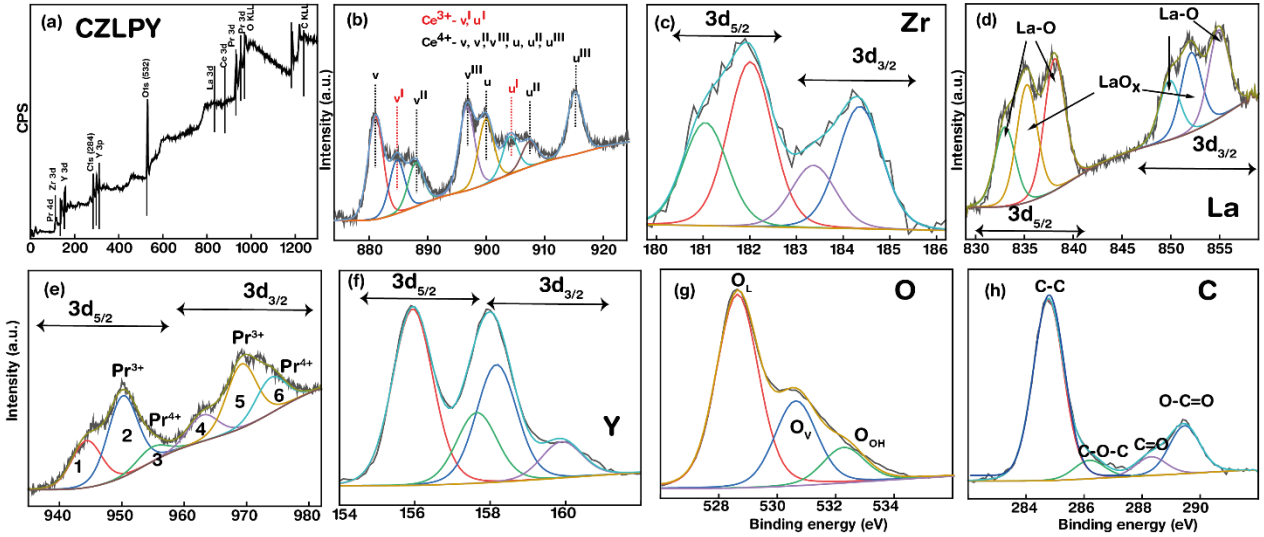
Homogeneity and elemental composition

BAND GAP



Estimated valence and conduction positions of HEOs with the position of redox potentials of water splitting reactions.

X-RAY PHOTOELECTRON SPECTROSCOPY



Presence of oxygen vacancies

Surface defects

Elemental composition

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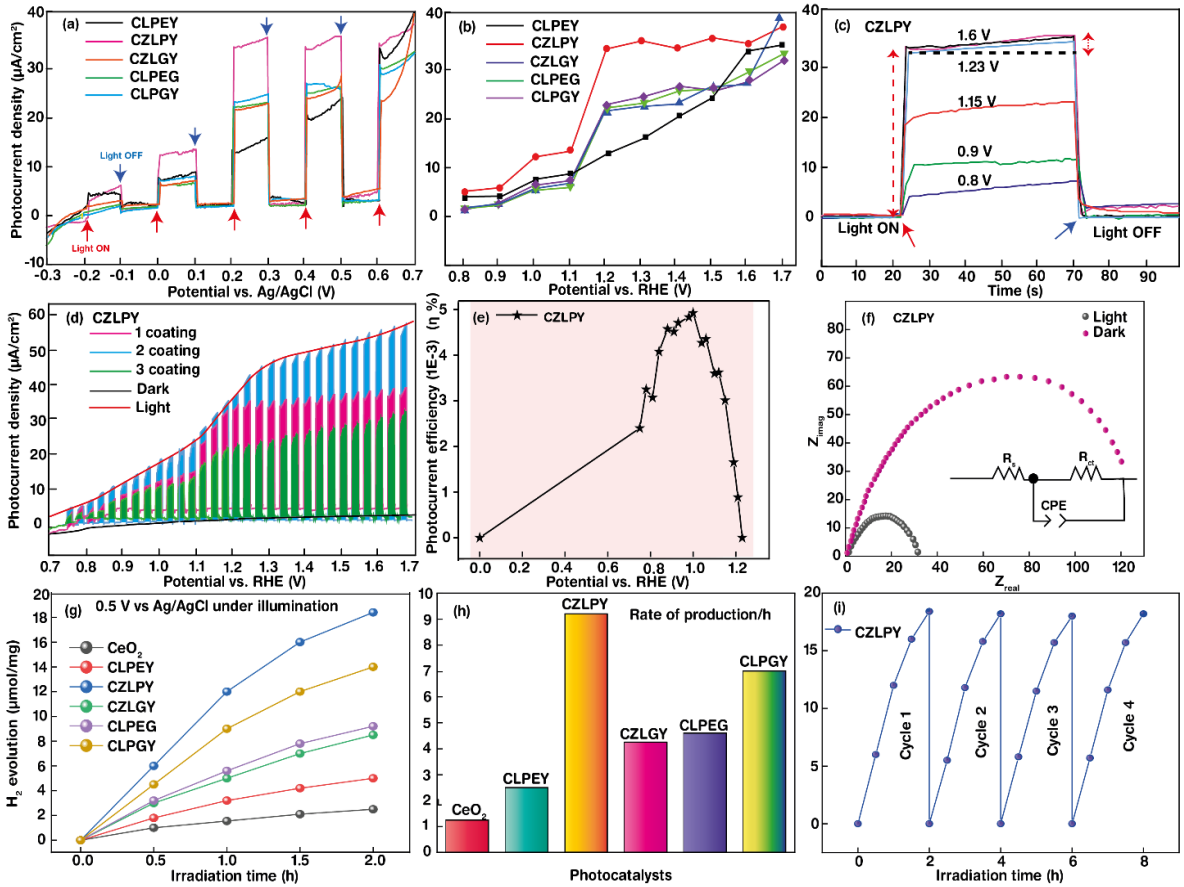
PHOTOELECTROCHEMICAL PERFORMANCE



Catalyst	H_2 generated [[μmolmg^{-1}] per hour]
CZLPY	9.2
CeO_2	0.8
ZnO	0.36*
3 wt% Y-ZnO	2.57*
3 wt% Ce – 3 wt% Y-ZnO	3.93*
25 wt%Y_2O_3 – TiO_2	1.38*

* Taken from literature

Catalyst	Surface $[O_V+O_H]/[O_V+O_H+O_L]$ (%)	HER activity in 2 hrs ($\mu mol mg^{-1}$)	Surface $[Pr^{3+}]/[Pr^{3+}+Pr^{4+}]$ (%)	Surface $[Ce^{3+}]/[Ce^{3+}+Ce^{4+}]$ (%)	D_{av} (nm)	ε_{av} ($\times 10^{-4}$)	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

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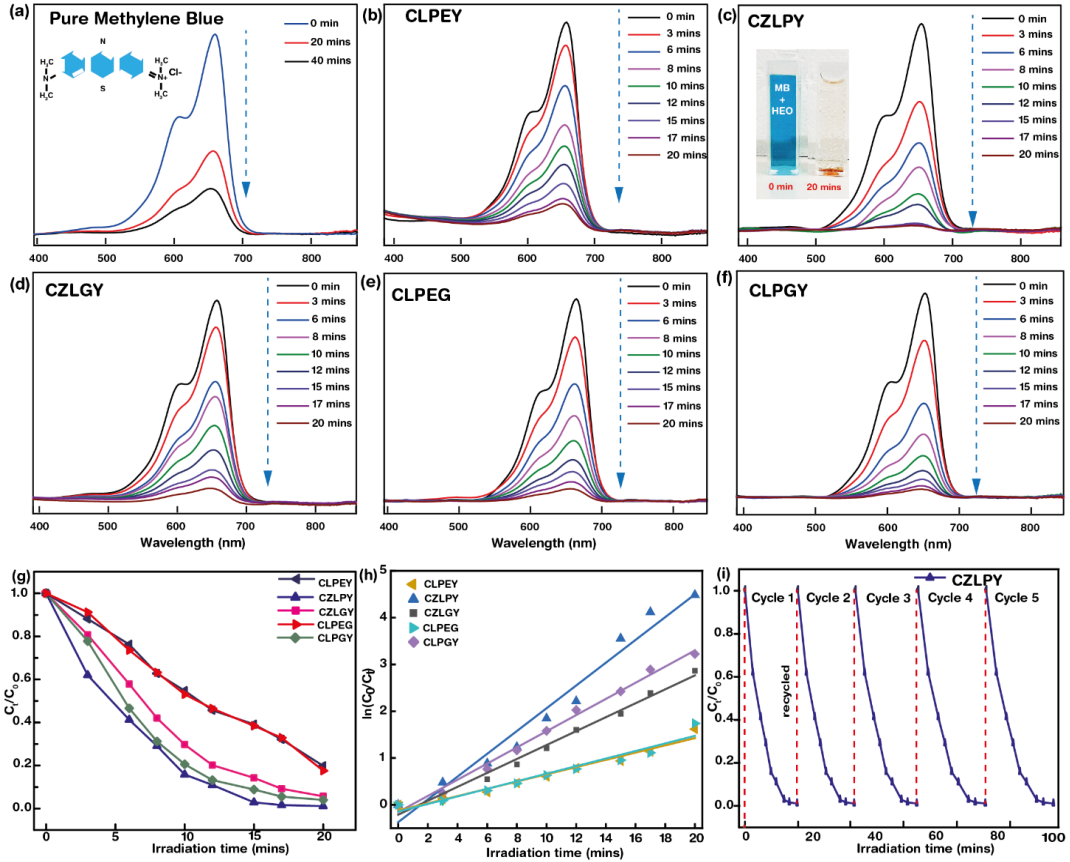
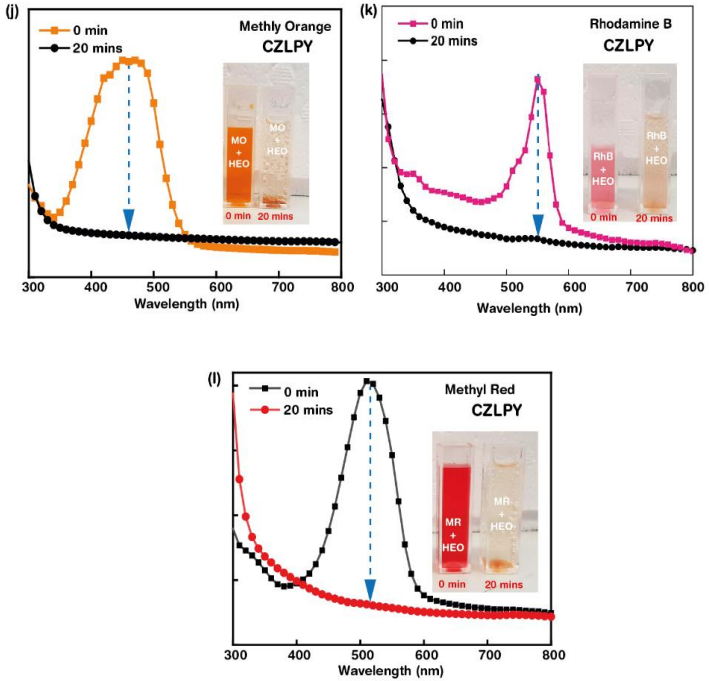
PHOTOCATALYTIC PERFORMANCE

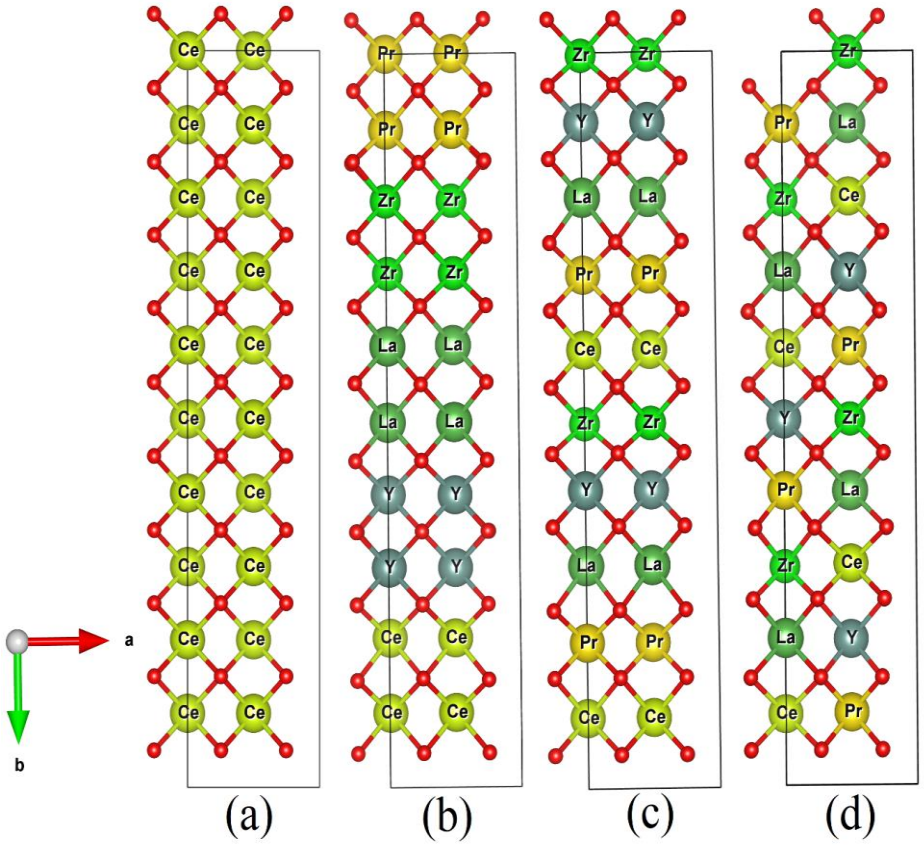

(a)
Pure Methylene Blue
0 min
20 mins
40 mins
(b)
CLPEY
(c)
CZLPY
MB + HEO
0 min
20 mins
(d)
CZLGY
(e)
CLPEG
(f)
CLPGY
Wavelength (nm)
(g)
CLPEY
CZLPY
CZLGY
CLPEG
CLPGY
Irradiation time (mins)
(h)
ln(C0/Ct)
Irradiation time (mins)
(i)
CZLPY
Cycle 1
Cycle 2
Cycle 3
Cycle 4
Cycle 5
recycled
Irradiation time (mins)


(j)
0 min
20 mins
Methly Orange
CZLPY
MO + HEO
0 min
20 mins
Wavelength (nm)
(k)
0 min
20 mins
Rhodamine B
CZLPY
RhB + HEO
0 min
20 mins
Wavelength (nm)
(l)
0 min
20 mins
Methyl Red
CZLPY
MR + HEO
0 min
20 mins
Wavelength (nm)

5

DFT: COMPUTATIONAL METHODOLOGY

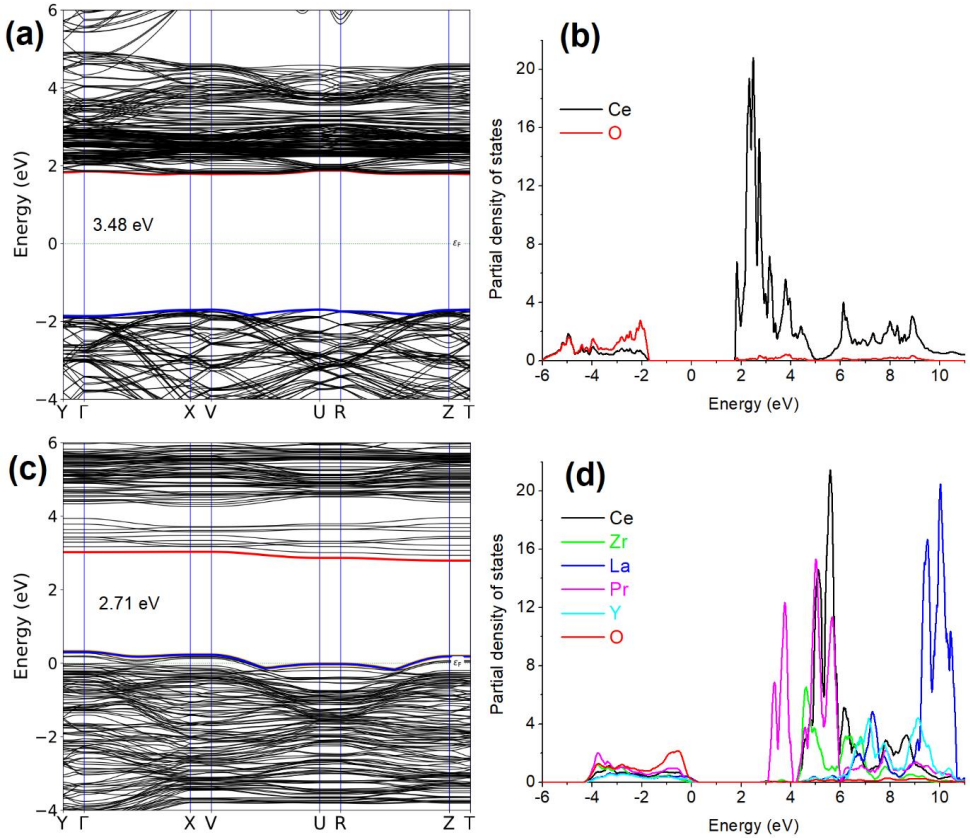
1x5x1 supercell of CeO_2 [(a)], along with [(b-d)] three possible models of Y, Pr, Zr, and La-doped 1x5x1 CeO_2 (CZLPY).

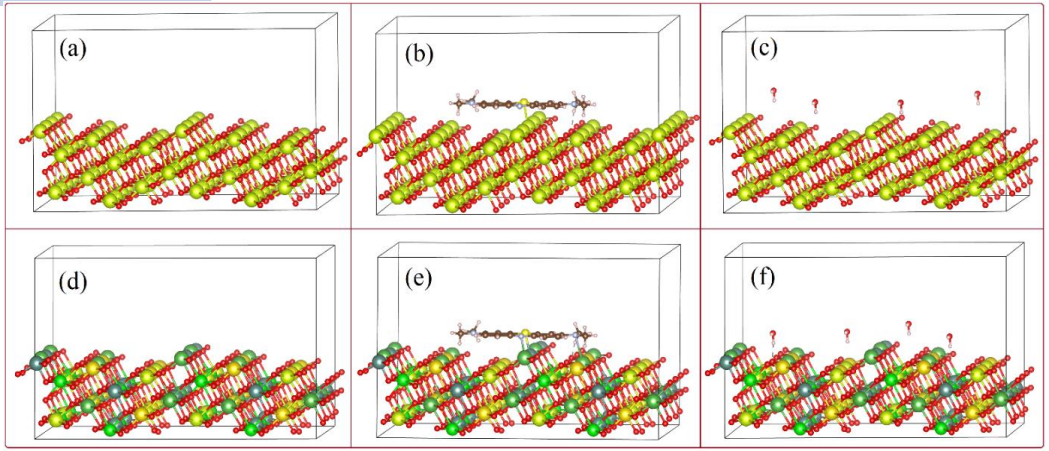


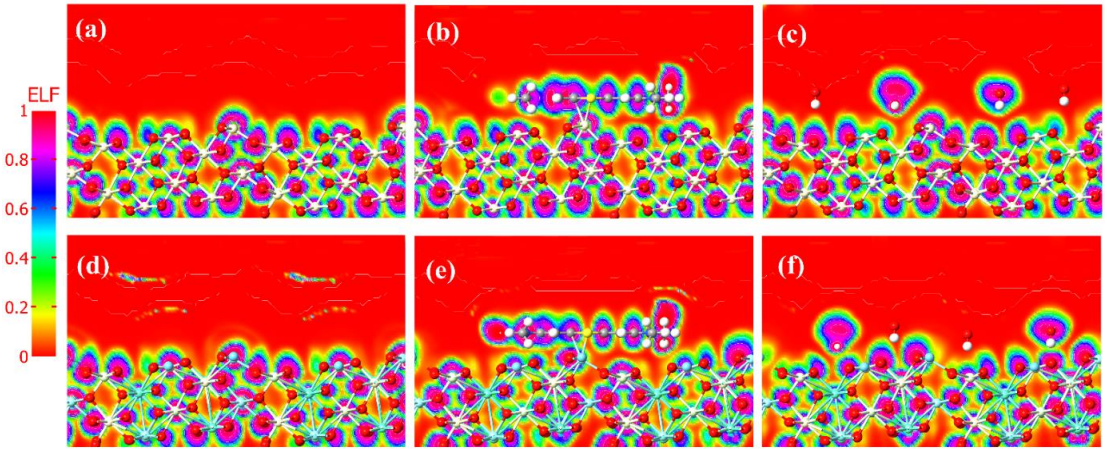
Species	Relative energy [eV]	Band gap [eV]
Pristine CeO_2	38641.65	3.48
Model 1	44569.27	0.93
Model 2	44571.35	0.65
Model 3	44573.94	2.71

Band structure along with PDOS plot of pristine 1x5x1 CeO_2 [a-b] and Model 3 [c-d].

The Fermi energy in all these plots is set to zero.





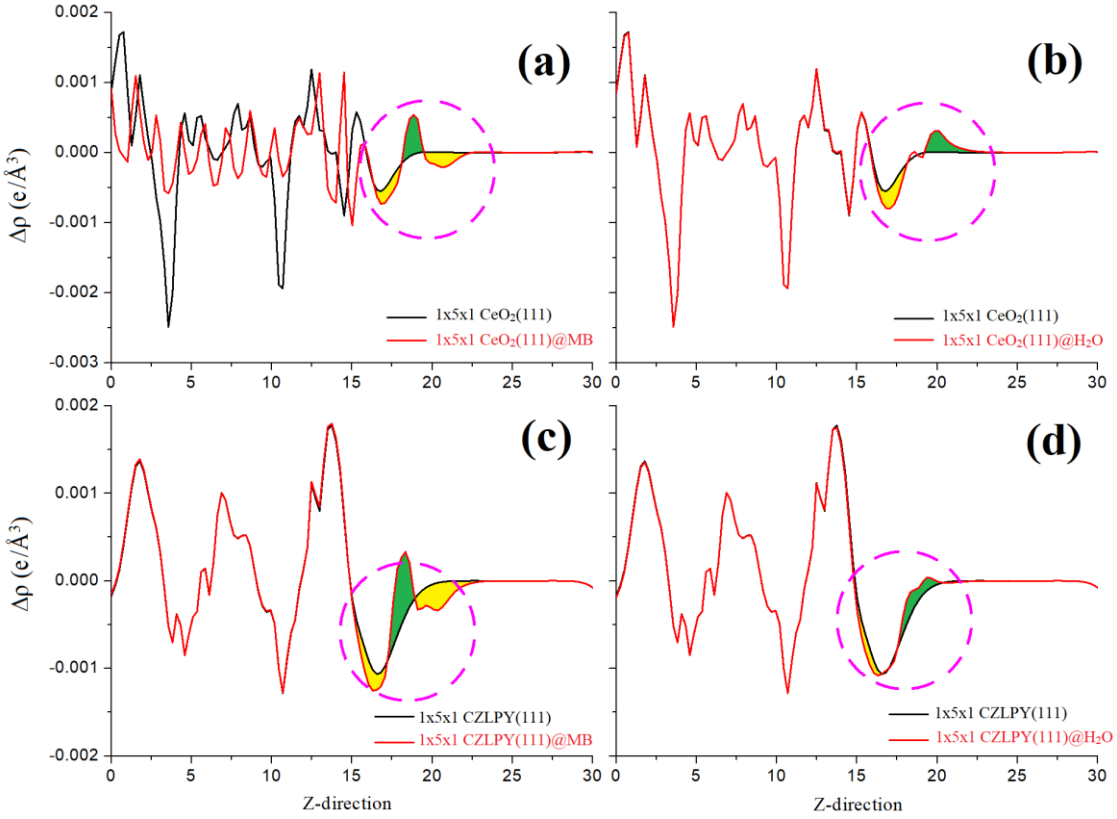


Relaxed geometry of (a) 1x5x1 CeO_2(111), (b) 1x5x1 CeO_2(111) @MB, (c) 1x5x1 CeO_2(111)@H_2O, (d) 1x5x1 CZLPY(111), (e) 1x5x1 CZLPY(111)@MB, and (f) 1x5x1 CZLPY(111)@H_2O interacting system.

Electron localization function map of a-f.

Average electron density difference (Δρ) 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.



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CONCLUSIONS

CONCLUSIONS

Synthesis

Successfull synthesis of five different rare-earth-based HEOs in equimolar 5-cation system.

Structure

Uniformly distributed elements incorporated within a single fluorite structure with lattice parameters similar as parent CeO_2.

Photocatalysis

CZLPY has shown the highest photocatalytic activity in AZO dyes degradation and photocatalytic water splitting in H_2 generation.

CZLPY

Presence of optimum level of Pr^{3+}, Ce^{3+} and the highest content of oxygen vacancies.

HEOs

The phase stabilization of HEO in parent CeO_2 lattice induced more lattice distortion, more Ce^{3+} concentration, more oxygen vacancies and additional energy levels as compared to pure CeO_2.

DFT

O anions are tetahedrally coordinated with 4 different 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.