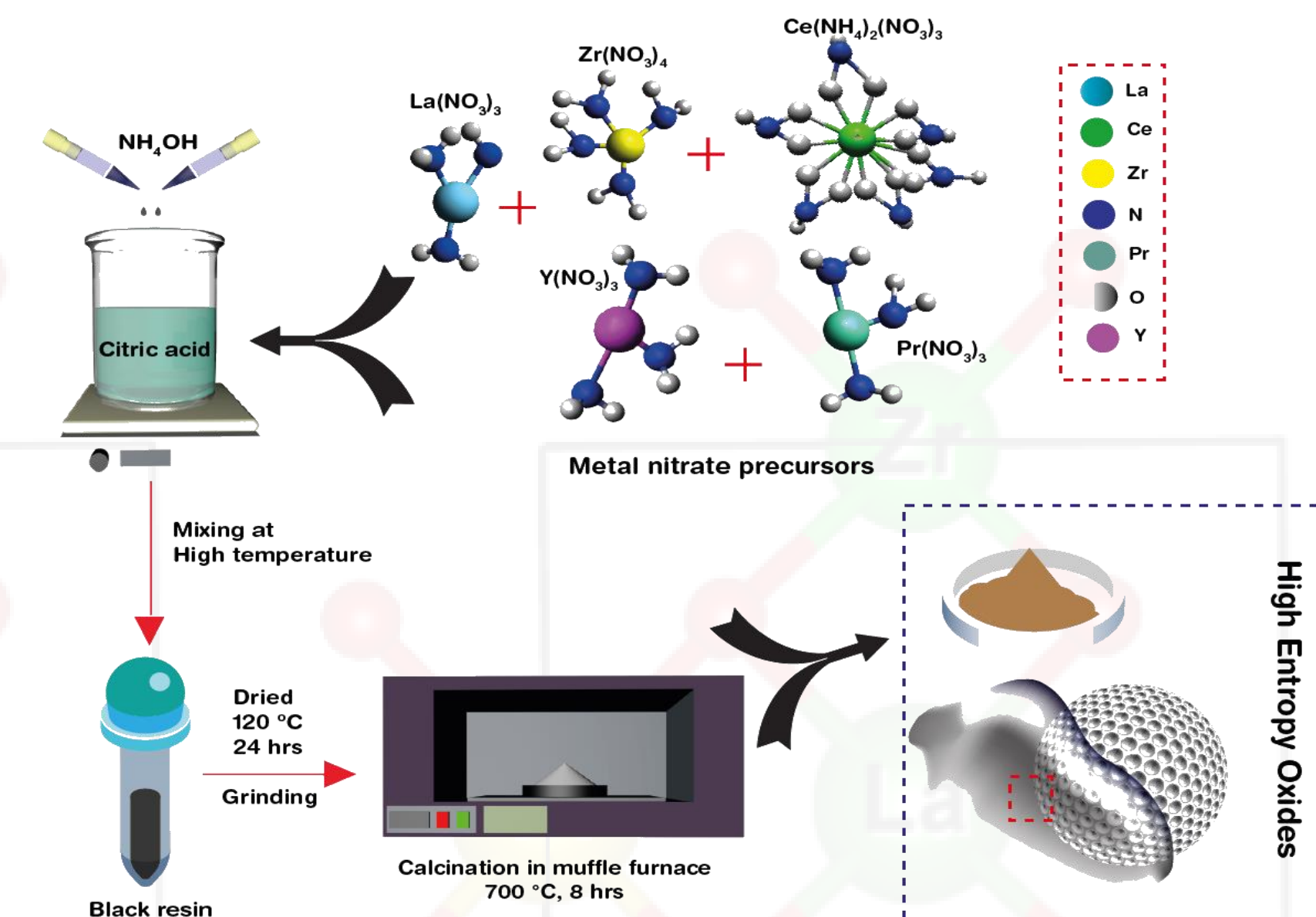


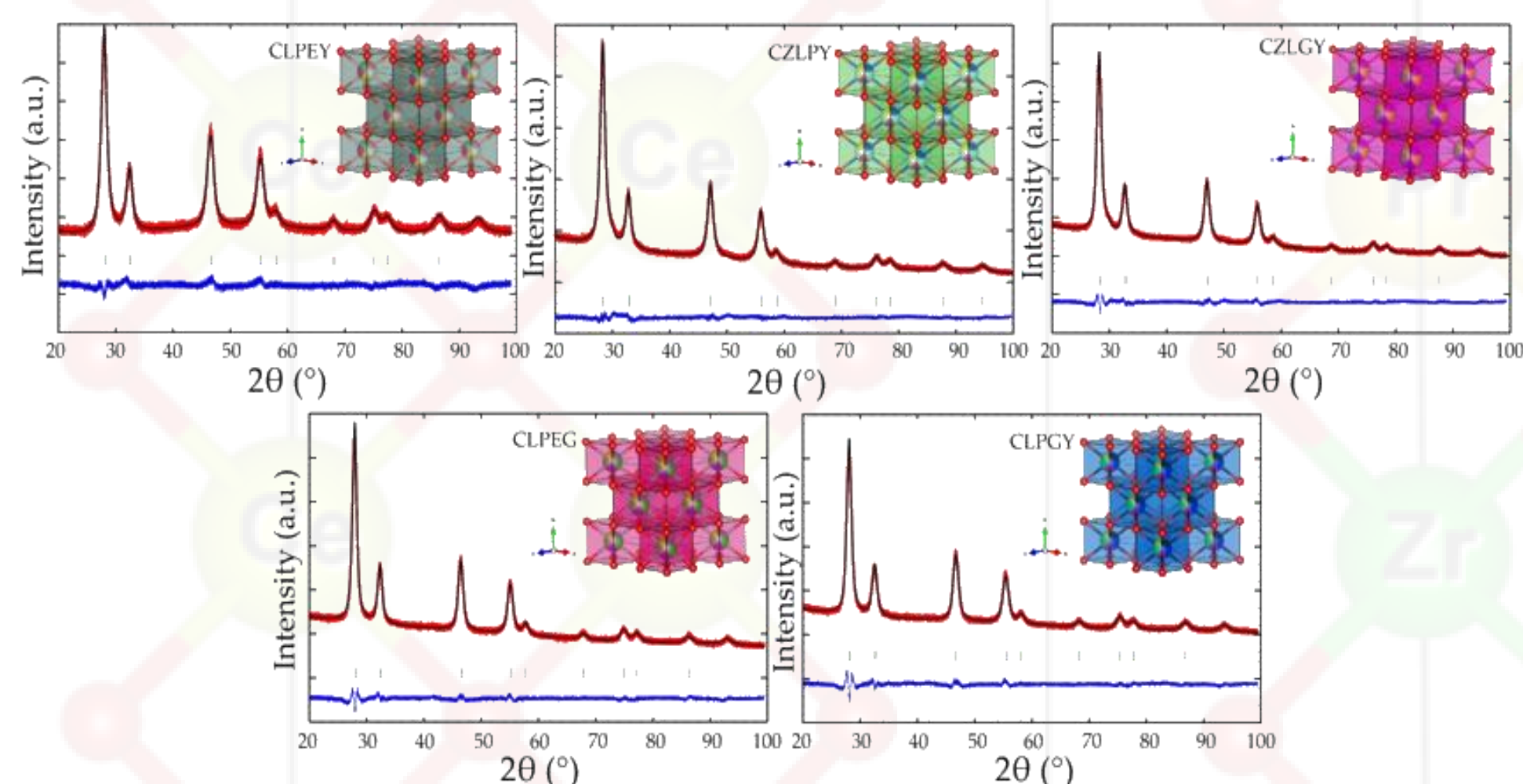
INTRODUCTION

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 $\text{Ce}_{0.2}\text{Zr}_{0.2}\text{La}_{0.2}\text{Pr}_{0.2}\text{Y}_{0.2}\text{O}_2$ (CZLPY) engender hydrogen in $9.2 \mu\text{mol mg}^{-1}$ per hour that is much higher content than for pristine CeO_2 material which amounts to $0.8 \mu\text{mol mg}^{-1}$ per hour.

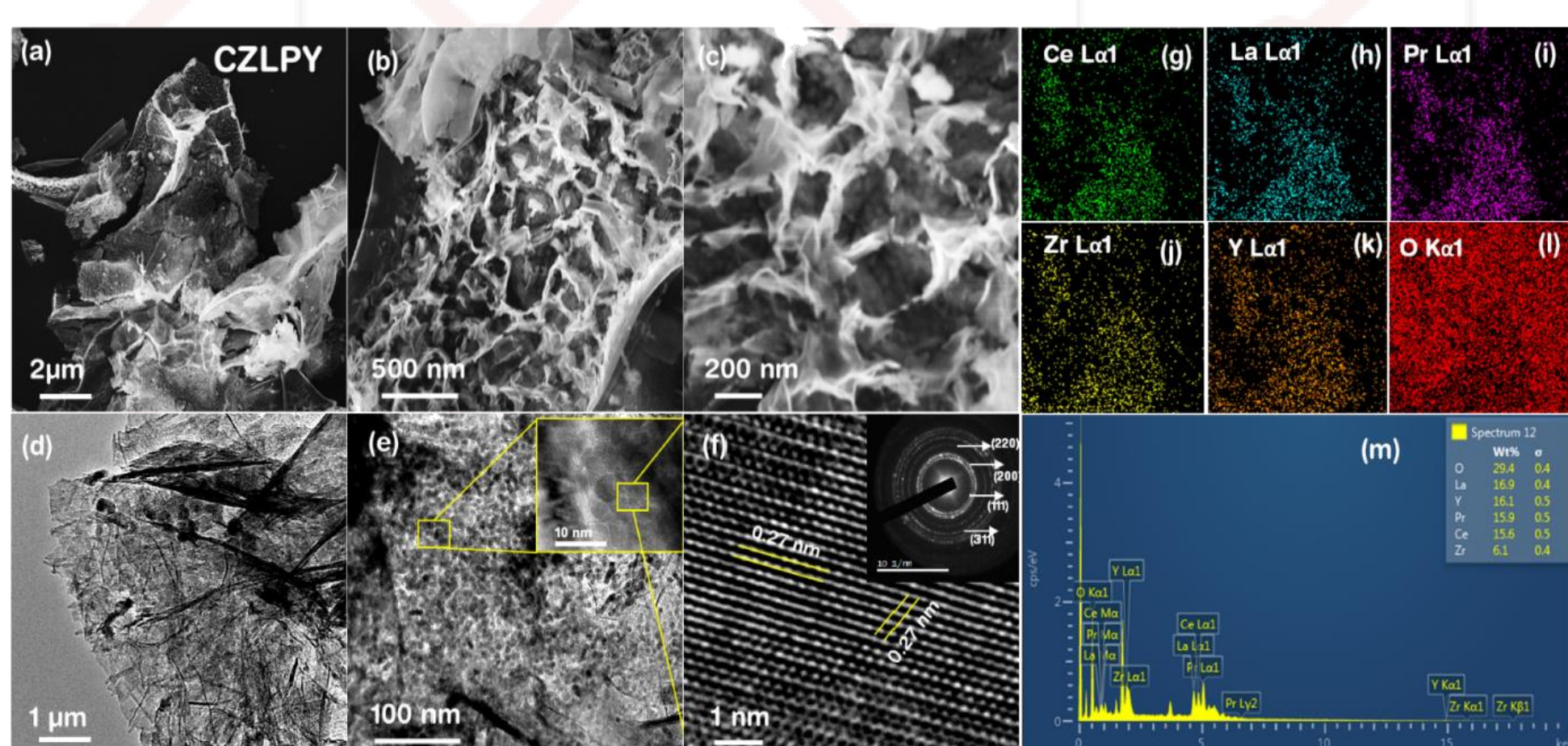
SOL-GEL SYNTHESIS



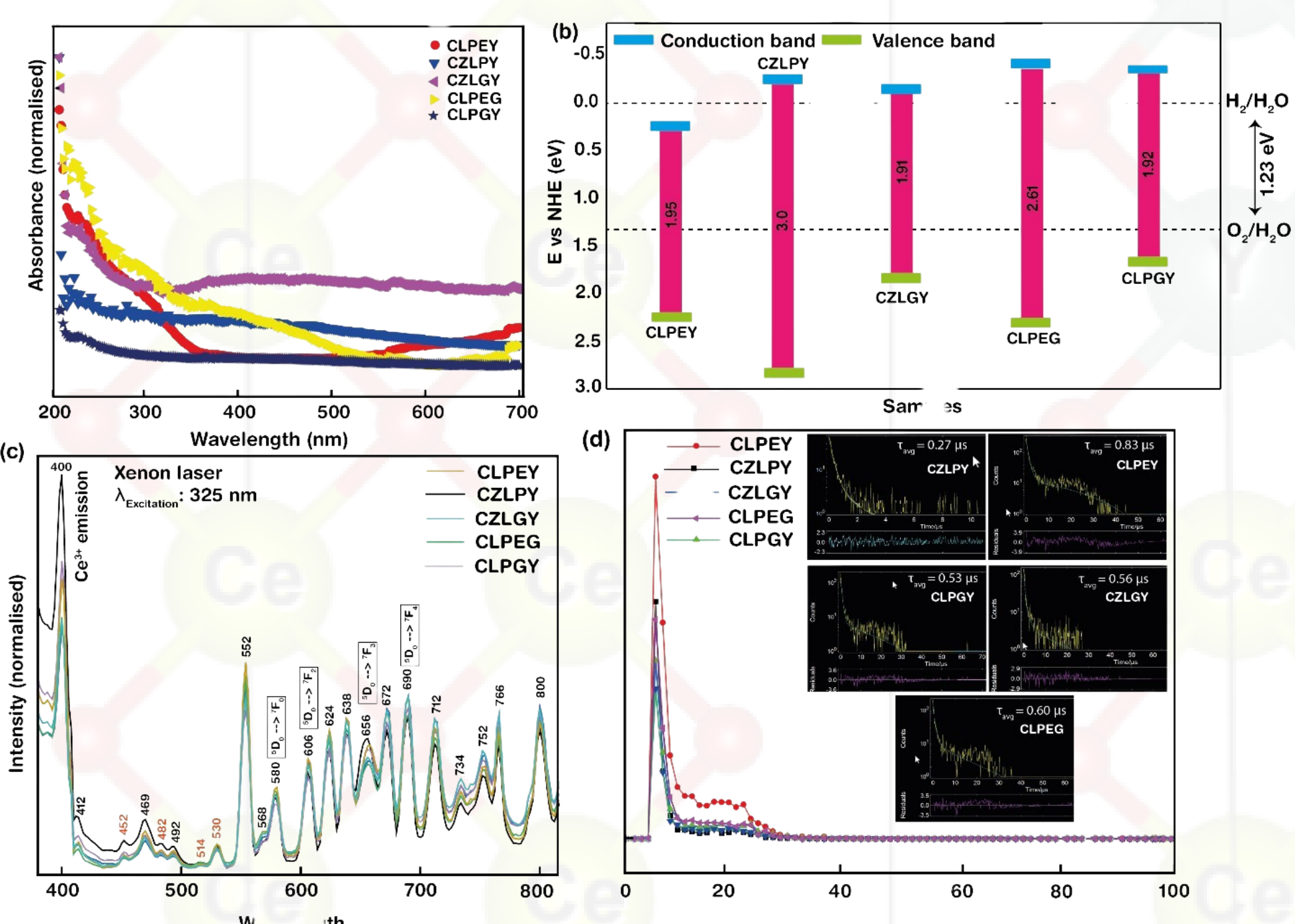
CHARACTERIZATION AND CATALYTIC ACTIVITY FOR AZO DYE DEGRADATION AND HYDROGEN EVOLUTION REACTION



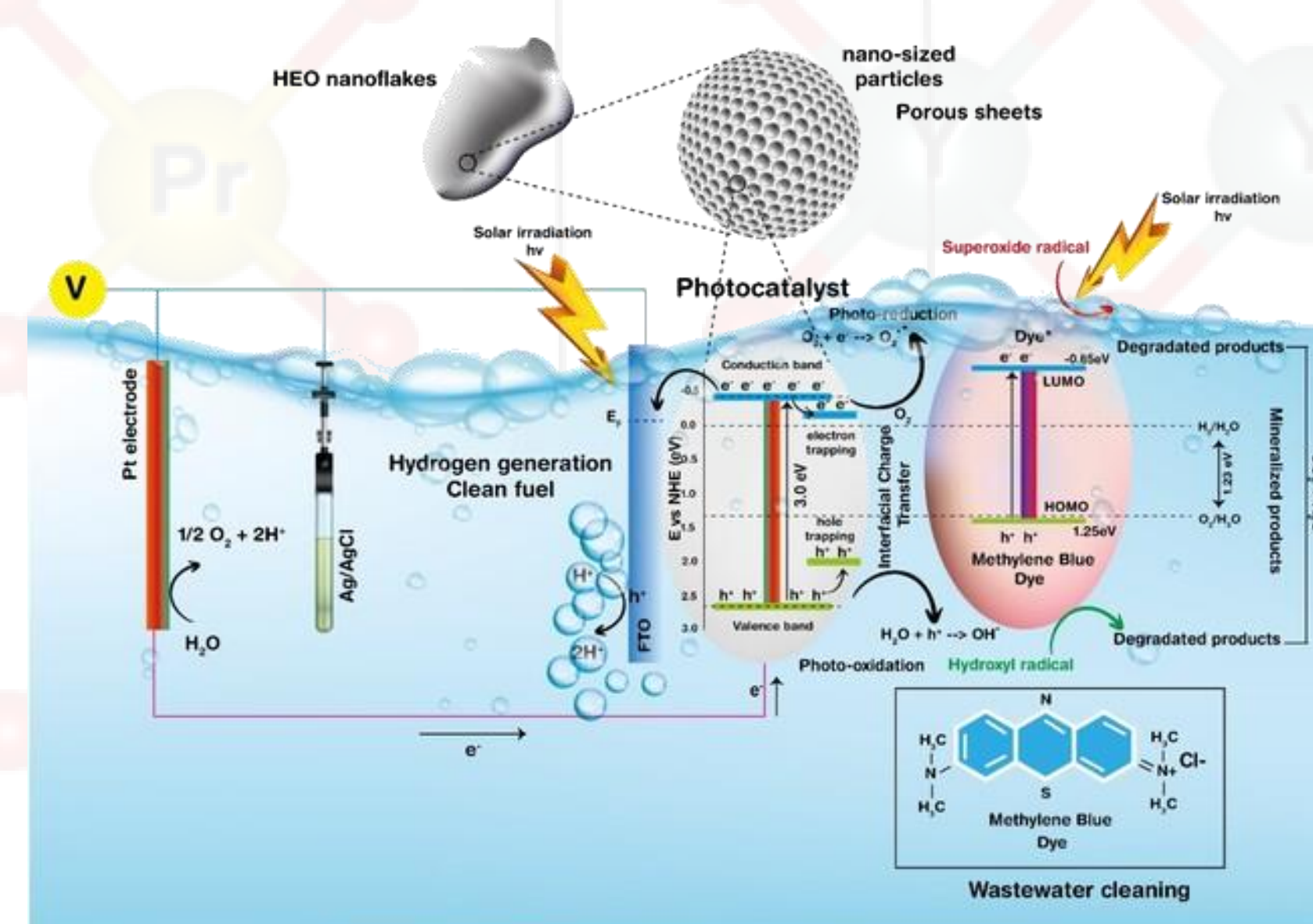
Rietveld plots of the investigated synthesized HEO catalysts with visualized fluorite-type crystal structure in the insets.



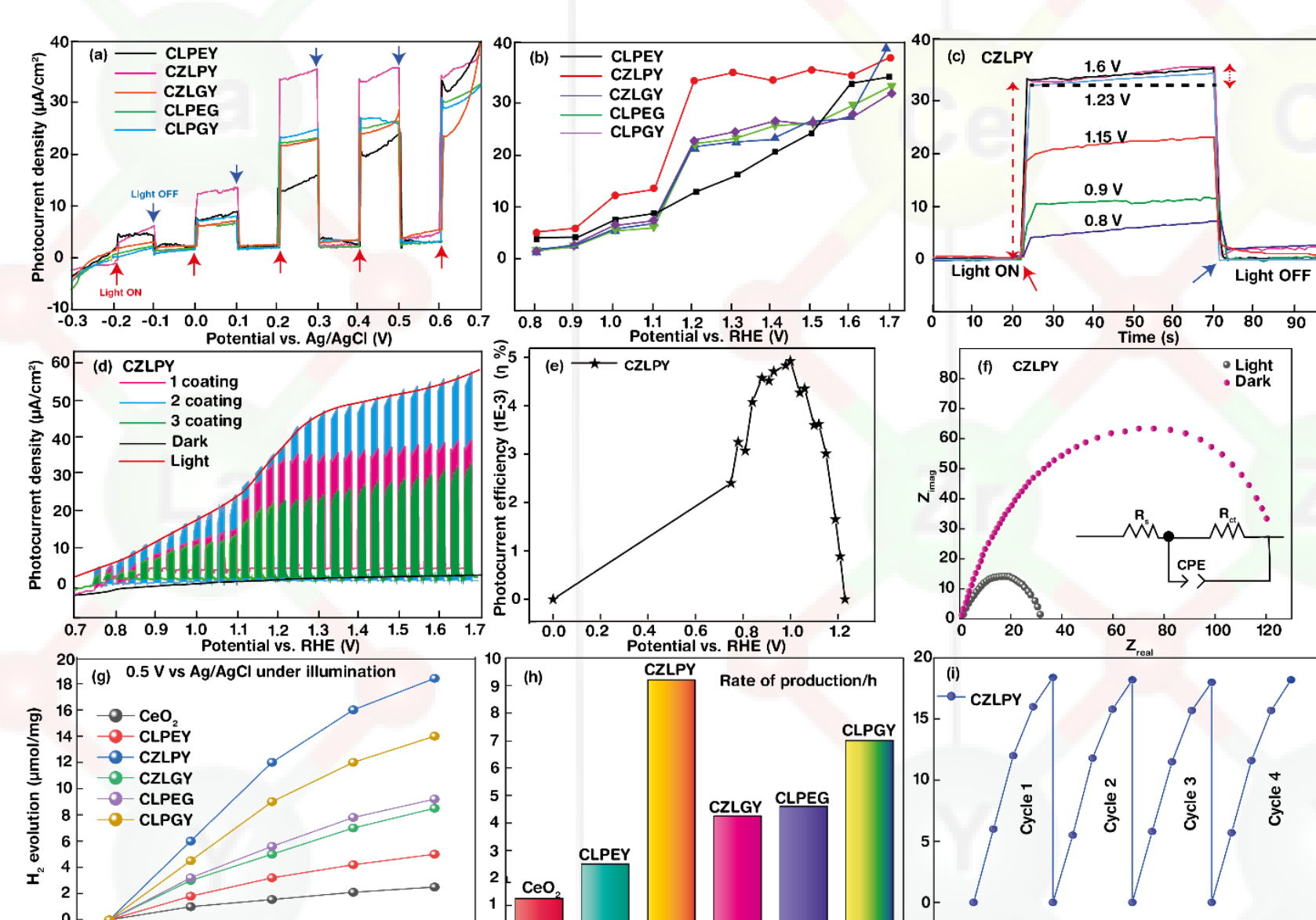
(a-c) Low and high magnification FE-SEM images of CZLPY catalyst; (d-e) TEM images of CZLPY catalyst with corresponding HR-TEM images displayed in the inset of (e) image and on the (f) image with SAED pattern shown in the inset of image (f); (g-l) Elemental maps of CZLPY; (m) EDS spectrum of CZLPY.



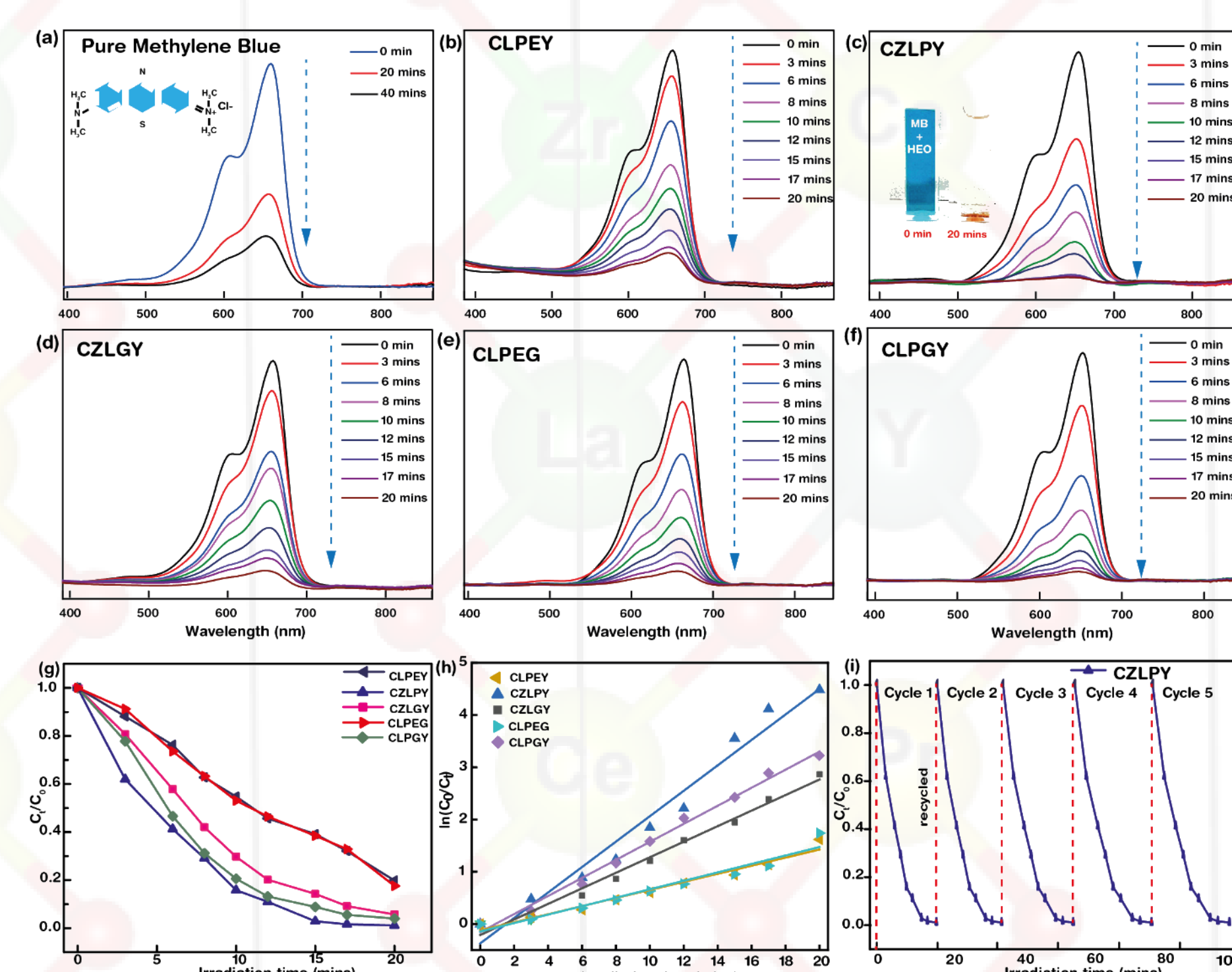
(a) Normalised absorption spectra for all as-synthesised HEOs; (b) Estimated valence and conduction positions of HEOs with the position of redox potentials of water splitting reactions; (c) Steady state PL spectra of HEOs; (d) Phosphorescence lifetime PL decays of HEOs using micro-flashlamp (μF_2) with inset showing bi-exponentially tail fitted decay profiles.



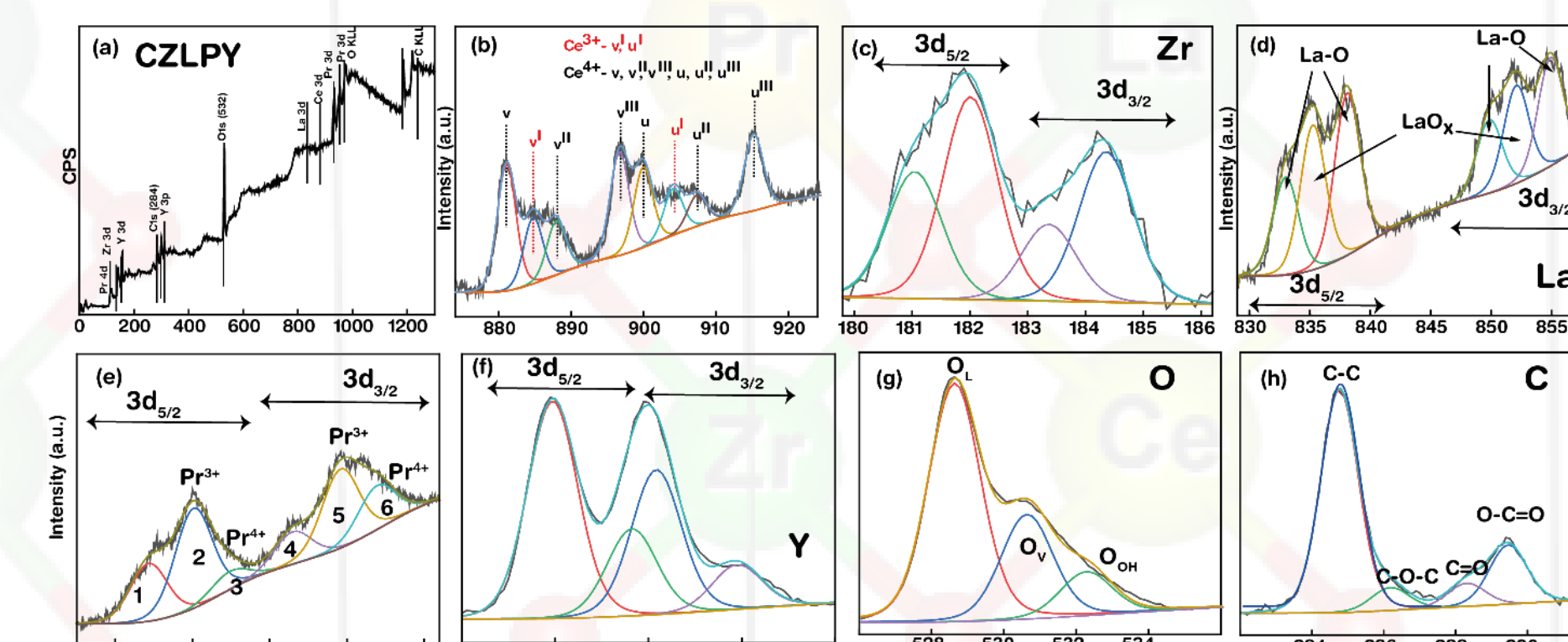
Schematic representation of the energy levels in HEOs with possible photocatalytic mechanism of MB degradation.



PEC performance of CLPEY, CZLPY, CZLGY, CLPEG, and CLPGY 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 at 0.8, 0.9, 1.15, 1.23 and 1.6 V vs. RHE (0.3 V vs. Ag/AgCl = 1.26 V vs. RHE); (d) LSV plots of CZLPY electrode with varied coating thickness (1,2,3) under chopped light and dark conditions (Potential vs. RHE); (e) Applied bias photon-to-current efficiency (ABPE, $\eta\%$) 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 (H_2) evolution by pure CeO_2 , CLPEY, CZLPY, CZLGY, CLPEG, and CLPGY 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.



UV-Vis absorption spectra of methylene blue (MB) dye under solar illumination (a) without and (b-f) with addition of HEOs monitored at regular interval of time. Inset showing colour degradation of MB dye to colourless solution after treatment with CZLPY and solar irradiation for 20 min; (g) The rate of photocatalytic degradation (C_0/C_t) of MB by HEOs under solar irradiation; (h) Plot of $\ln(C_0/C_t)$ vs irradiation time; (i) Re-cyclability test of CZLPY towards MB dye degradation.



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.

Catalyst	Surface $[\text{O}_\text{V}+\text{O}_\text{H}]/[\text{O}_\text{V}+\text{O}_\text{H}+\text{O}_\text{L}]$ (%)	HER activity in 2 hrs ($\mu\text{mol mg}^{-1}$)	Surface $[\text{Pr}^{3+}]/[\text{Pr}^{3+}+\text{Pr}^{4+}]$ (%)	Surface $[\text{Ce}^{3+}]/[\text{Ce}^{3+}+\text{Ce}^{4+}]$ (%)	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

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 CeO_2 . The variation of equimolar chemical composition yielded the band gap variation and modulation of electronic structure. Among studied HEOs, $\text{Ce}_{0.2}\text{Zr}_{0.2}\text{La}_{0.2}\text{Pr}_{0.2}\text{Y}_{0.2}\text{O}_2$ (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.