

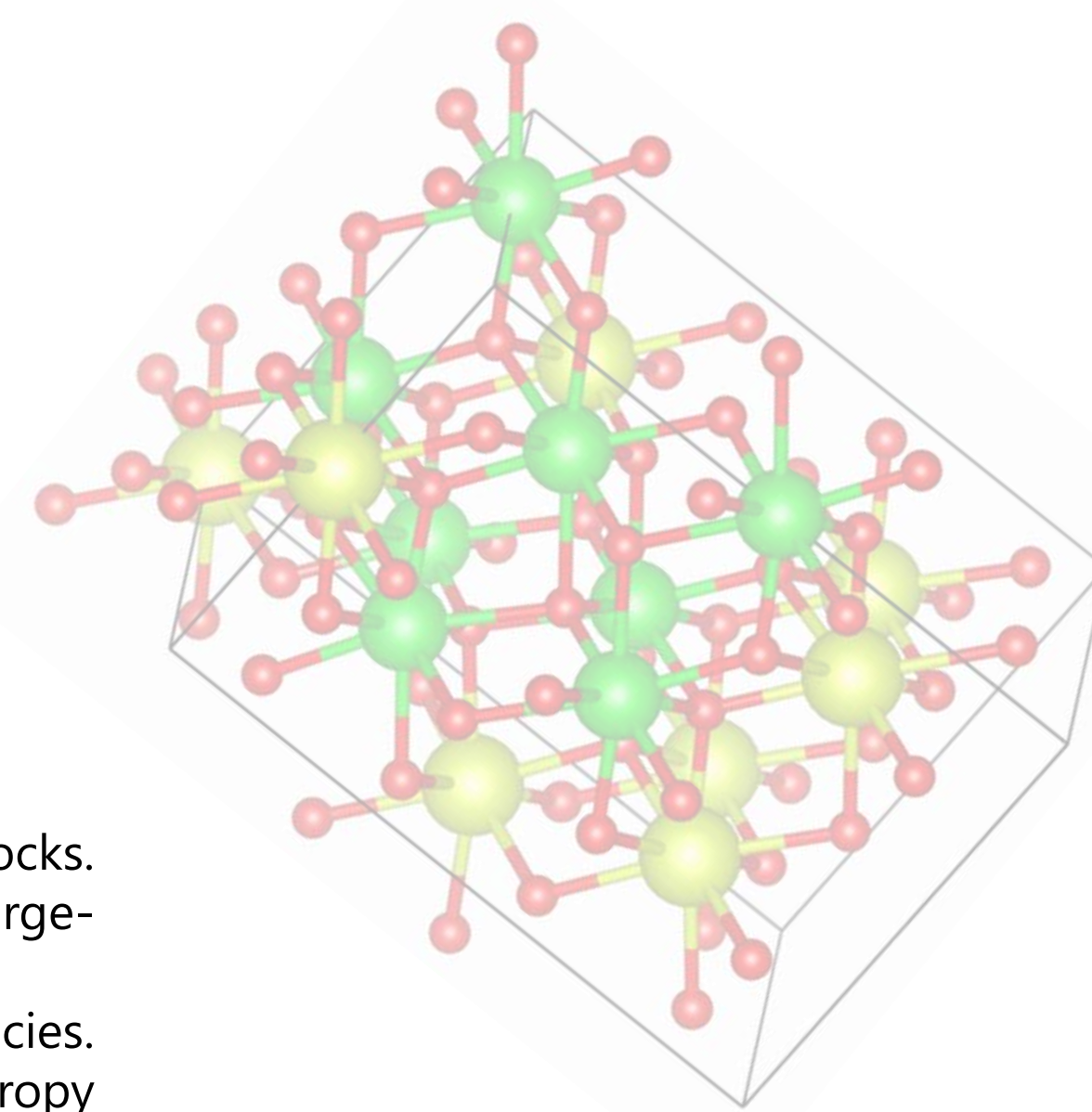


Visible-light-assisted reduction of carbon dioxide catalyzed by ordered and disordered ceria-zirconia-based structures

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INTRODUCTION

The photocatalytic conversion of CO₂ into value-added chemicals using solar energy offers a promising approach to reducing greenhouse gas emissions while producing sustainable fuels and chemical feedstocks. However, the activation of the chemically stable CO₂ molecule under visible light remains challenging and requires photocatalysts with tailored electronic structures, suitable surface properties, and efficient charge-transfer characteristics.

Ceria-zirconia-based oxides are promising materials for CO₂ conversion owing to their excellent redox properties, high oxygen storage capacity, oxygen mobility, and ability to accommodate oxygen vacancies. These features play an important role in CO₂ adsorption and activation, as well as in the stabilization and transformation of surface intermediates. Incorporating multiple rare-earth cations through a high-entropy oxide (HEO) approach offers an additional strategy for tuning the local structure, defect chemistry, and redox behavior of ceria-zirconia systems.[1]

In this work, six ordered and disordered ceria-zirconia-based oxides were synthesized using a controlled citrate sol-gel route. Thermal treatment enabled the formation of different structural motifs, including solid-solution, pyrochlore, κ -phase, and partially oxidized phases. Their structural, surface, and electronic properties were systematically investigated and correlated with photocatalytic CO₂ hydrogenation under visible light. Density functional theory (DFT) calculations were further employed to elucidate the influence of structural disorder on CO₂ adsorption, product binding, and the resulting photocatalytic performance. [2]

RESULTS

Table 1. List of prepared compound acronyms along with their chemical formula.

Compound code name	Chemical formula
CeZrO	Ce _{0.5} Zr _{0.5} O _{2-δ}
LCPGY	La _{0.1} Ce _{0.1} Pr _{0.1} Gd _{0.1} Y _{0.1} Zr _{0.5} O _{2-δ}
pyr-CeZrO	Ce ₂ Zr ₂ O ₇
dp-LCPGY	(La _{0.2} Ce _{0.2} Pr _{0.2} Gd _{0.2} Y _{0.2}) ₂ Zr ₂ O _{7-δ} + La _{0.1} Ce _{0.1} Pr _{0.1} Gd _{0.1} Y _{0.1} Zr _{0.5} O _{2-δ}
κ -CeZrO	Ce ₂ Zr ₂ O ₈
part. ox. pyr-LCPGY	(La _{0.2} Ce _{0.2} Pr _{0.2} Gd _{0.2} Y _{0.2}) ₂ Zr ₂ O _{7-δ}

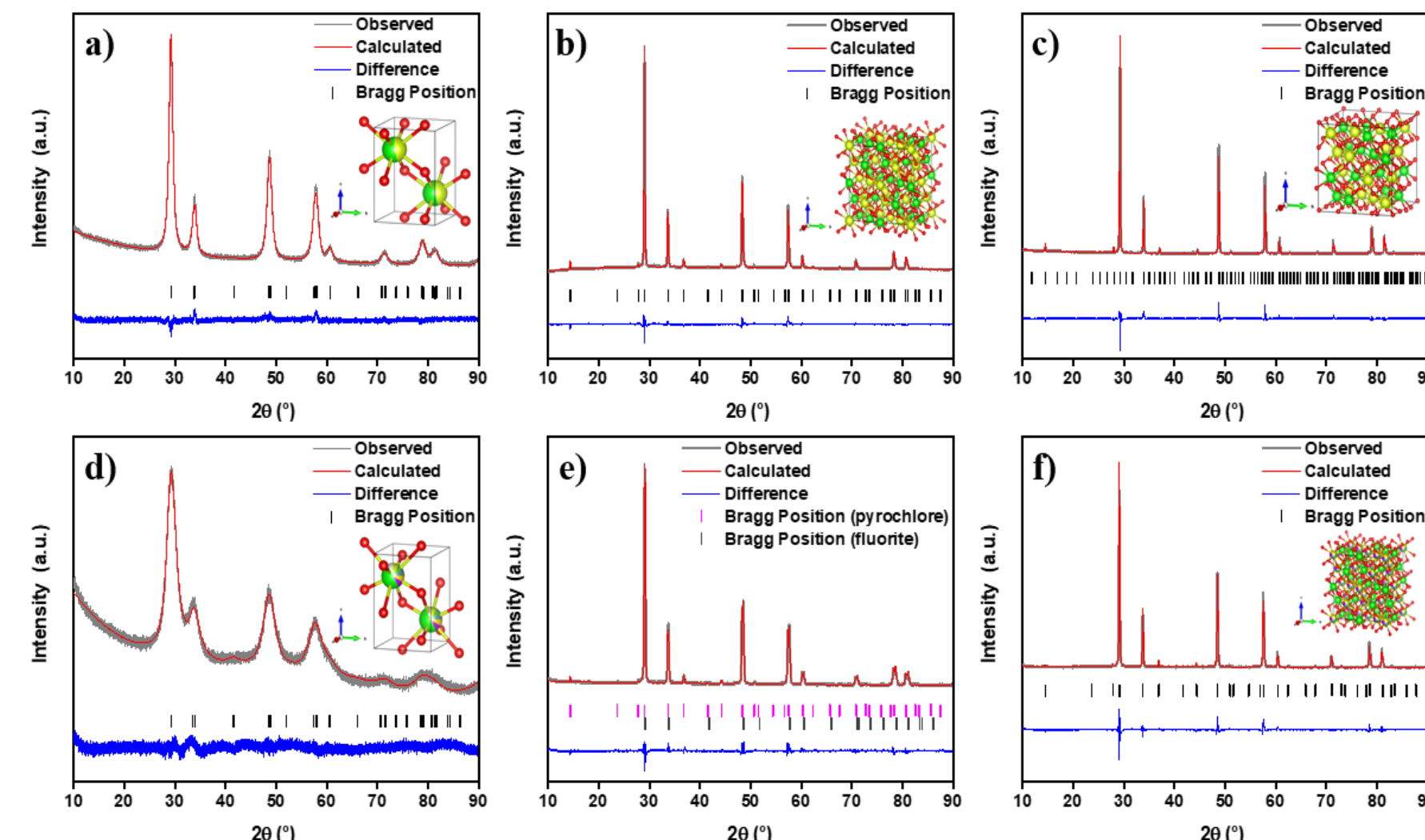


Figure 1. Rietveld output plots of a) CeZrO, b) pyr-CeZrO, c) κ -CeZrO, d) LCPGY, e) dp-LCPGY, and f) partially oxidized pyr-LCPGY.

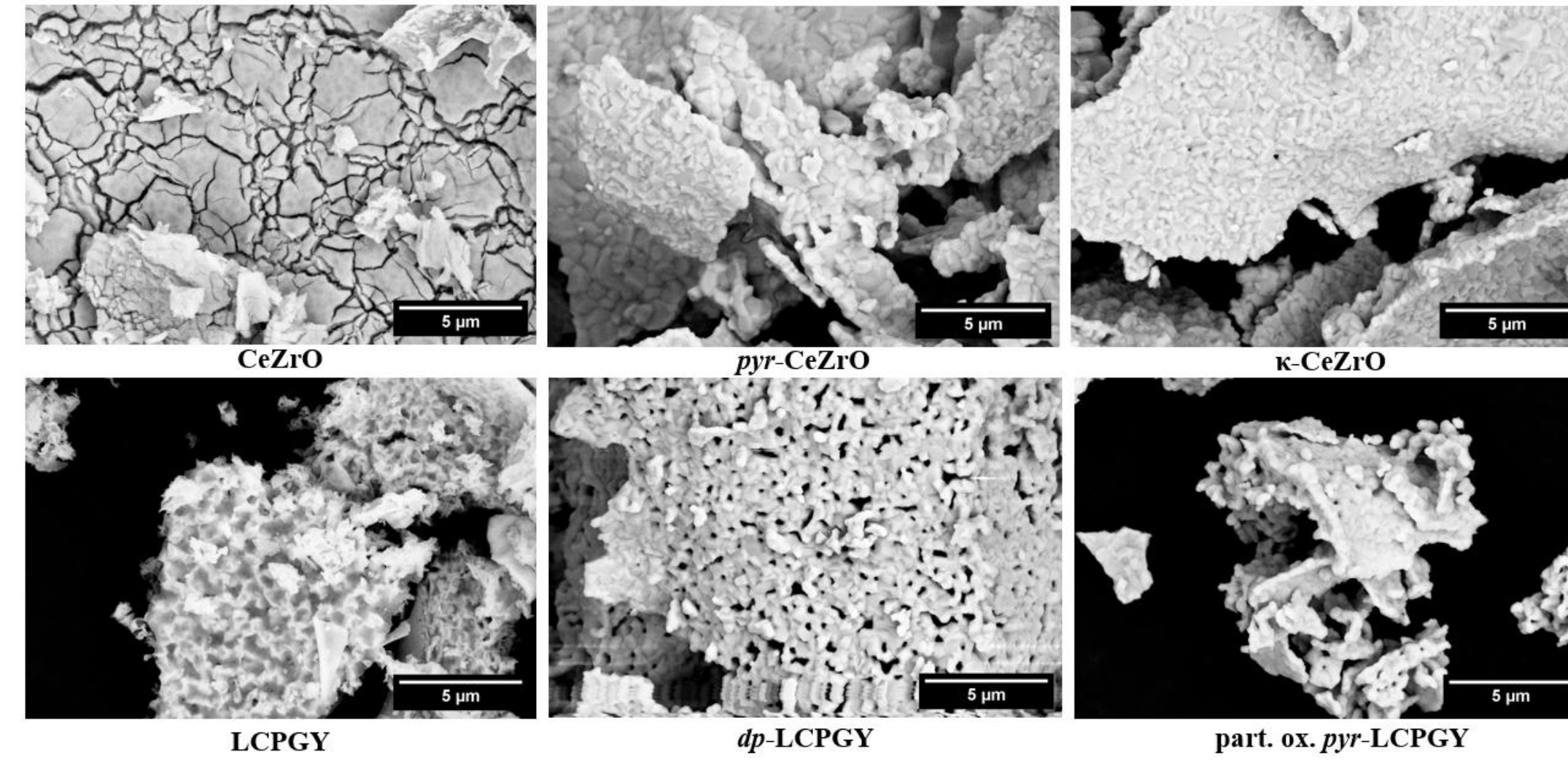


Figure 2. SEM images of CeZrO, pyr-CeZrO, κ -CeZrO, LCPGY, dp-LCPGY and partially oxidized pyr-LCPGY powders.

Table 2. Overview of the results of photocatalytic CO₂ hydrogenation.

Code name	CO ₂ conversion (%)	Selectivity (%)	
		CO	HCHO
CeO ₂	6.06	100	-
ZrO ₂	7.34	100	-
CeZrO	9.78	100	-
pyr-CeZrO	15.04	100	-
κ -CeZrO	20.75	100	-
LCPGY	11.99	100	-
dp-LCPGY	24.15	89.98	10.02
part.ox. pyr-LCPGY	21.77	94.78	5.22

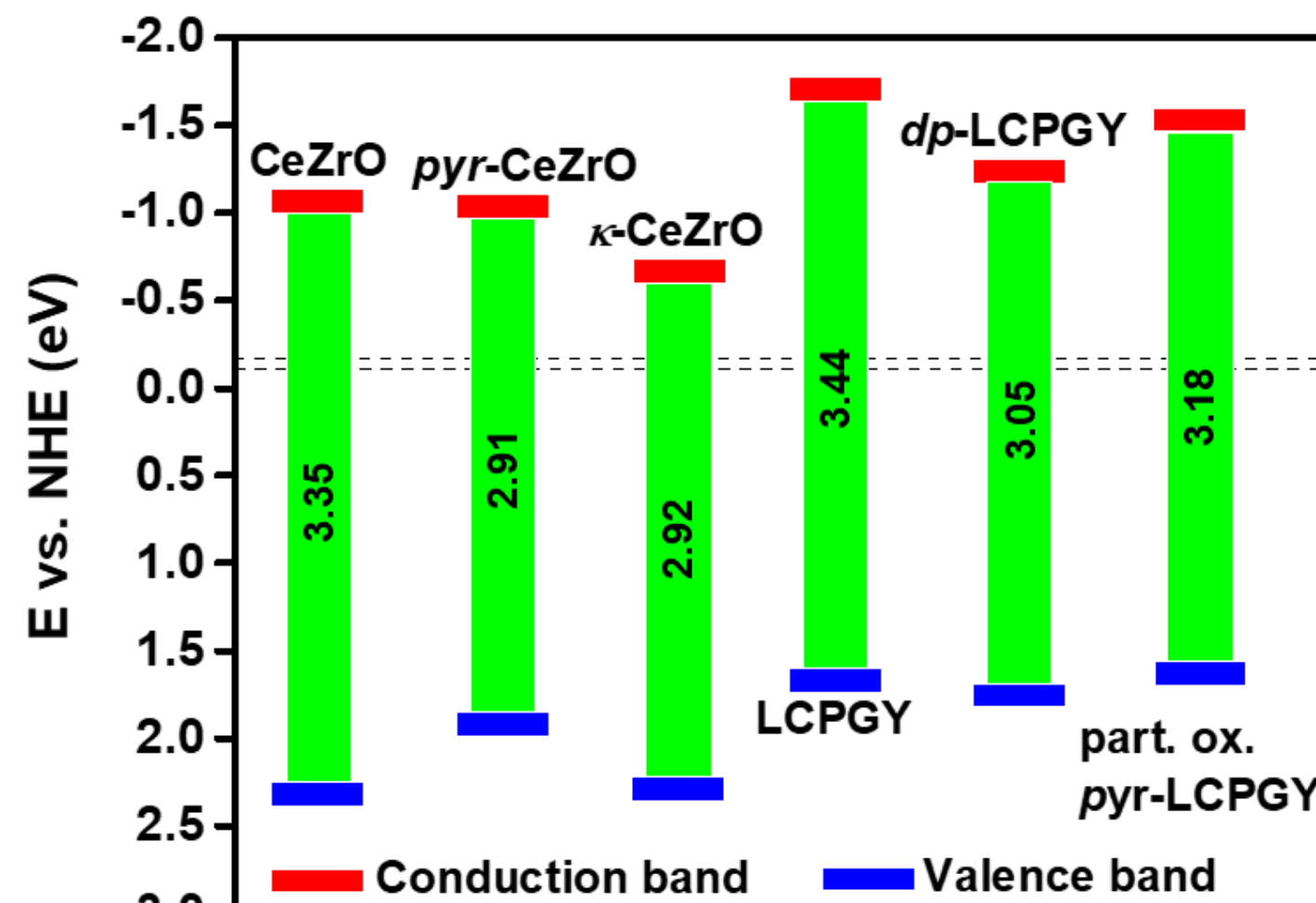


Figure 3. Estimated conduction and valence band positions of catalysts with the positions of redox potentials of CO₂ reduction reactions.

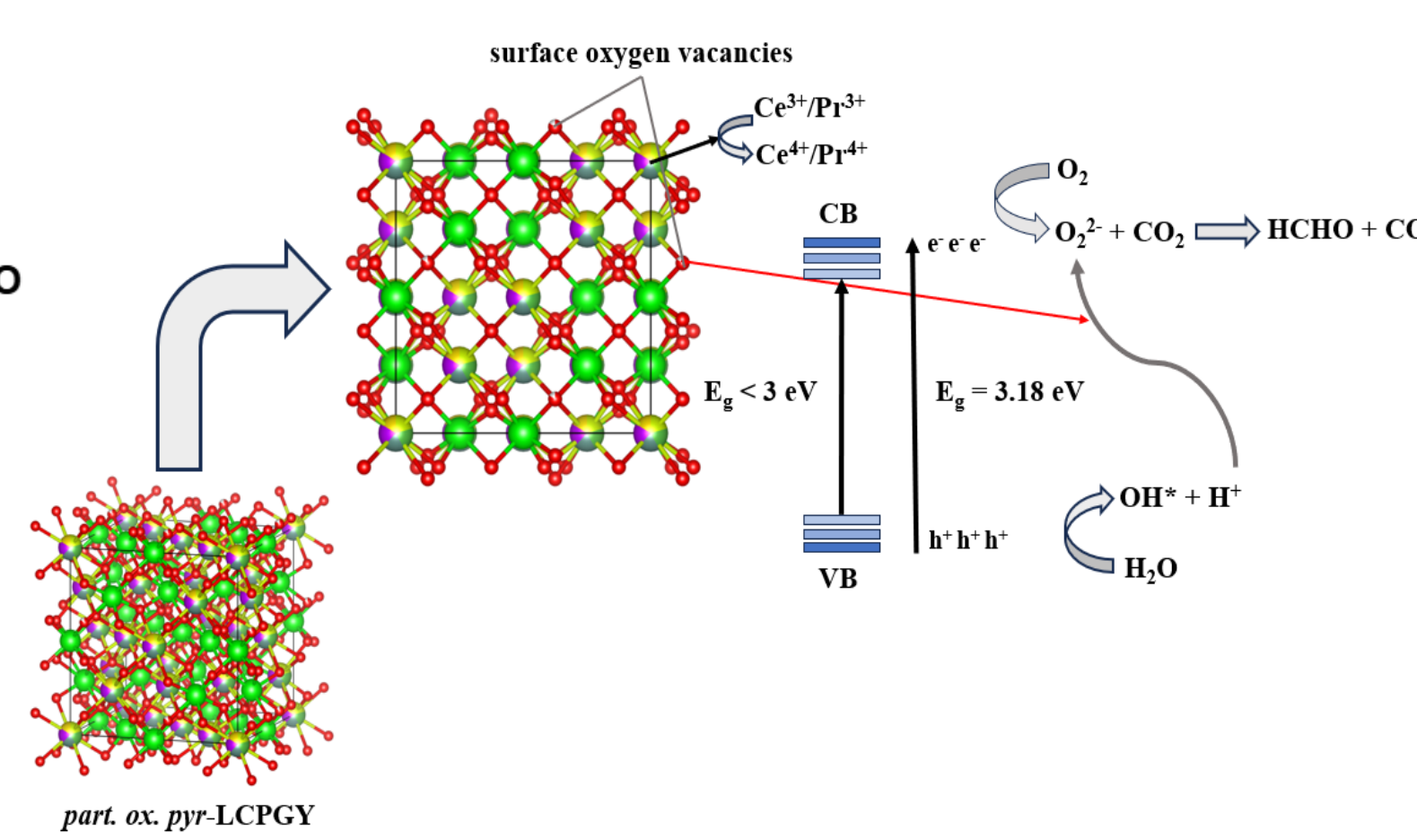


Figure 4. Schematic representation of the photocatalytic mechanism of CO₂ hydrogenation.

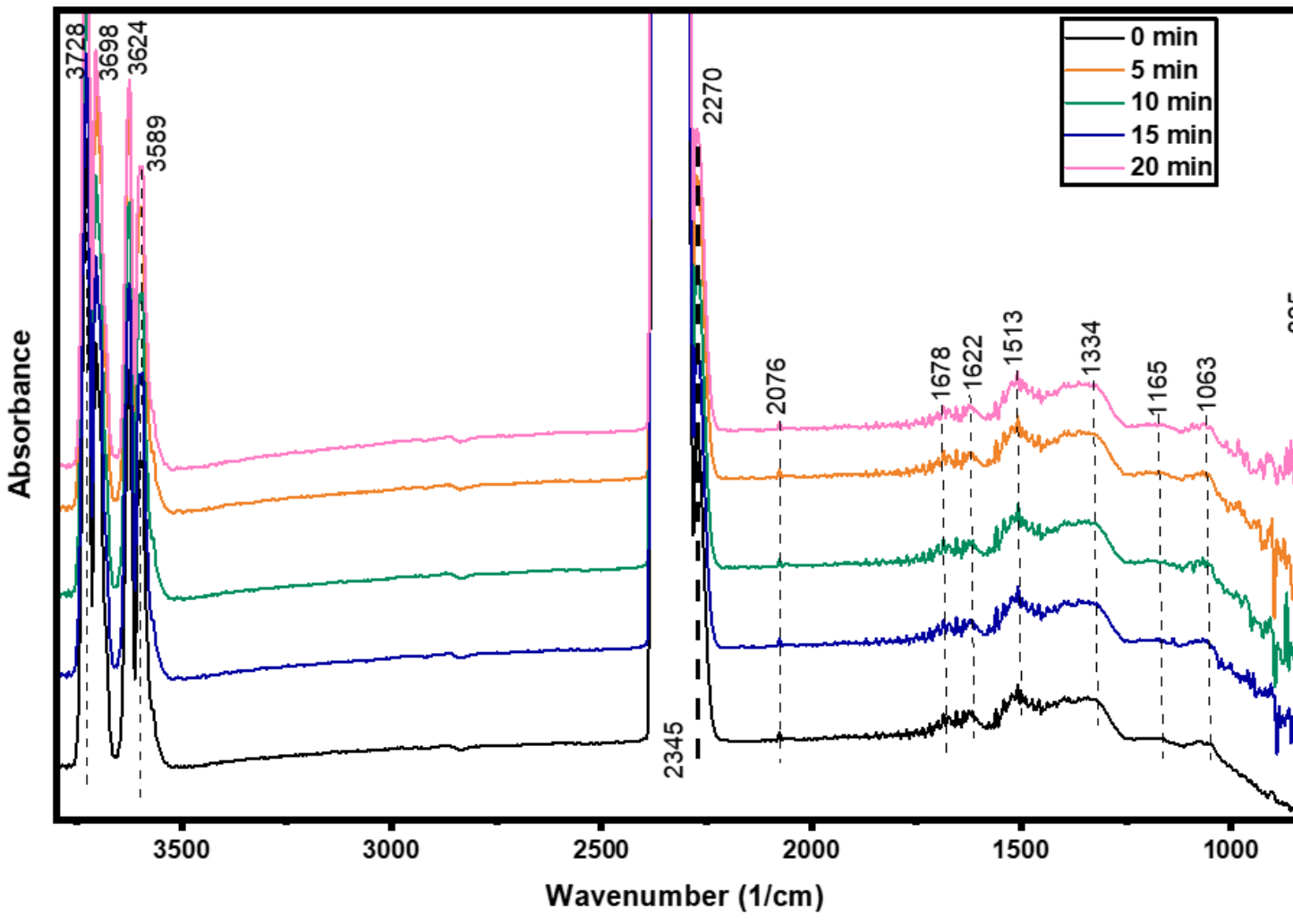


Figure 5. Complete in situ DRIFTS spectra of part. ox. pyr-LCPGY conducted at 0 min, 5 min, 10 min, 15 min, and 20 min of light irradiation.

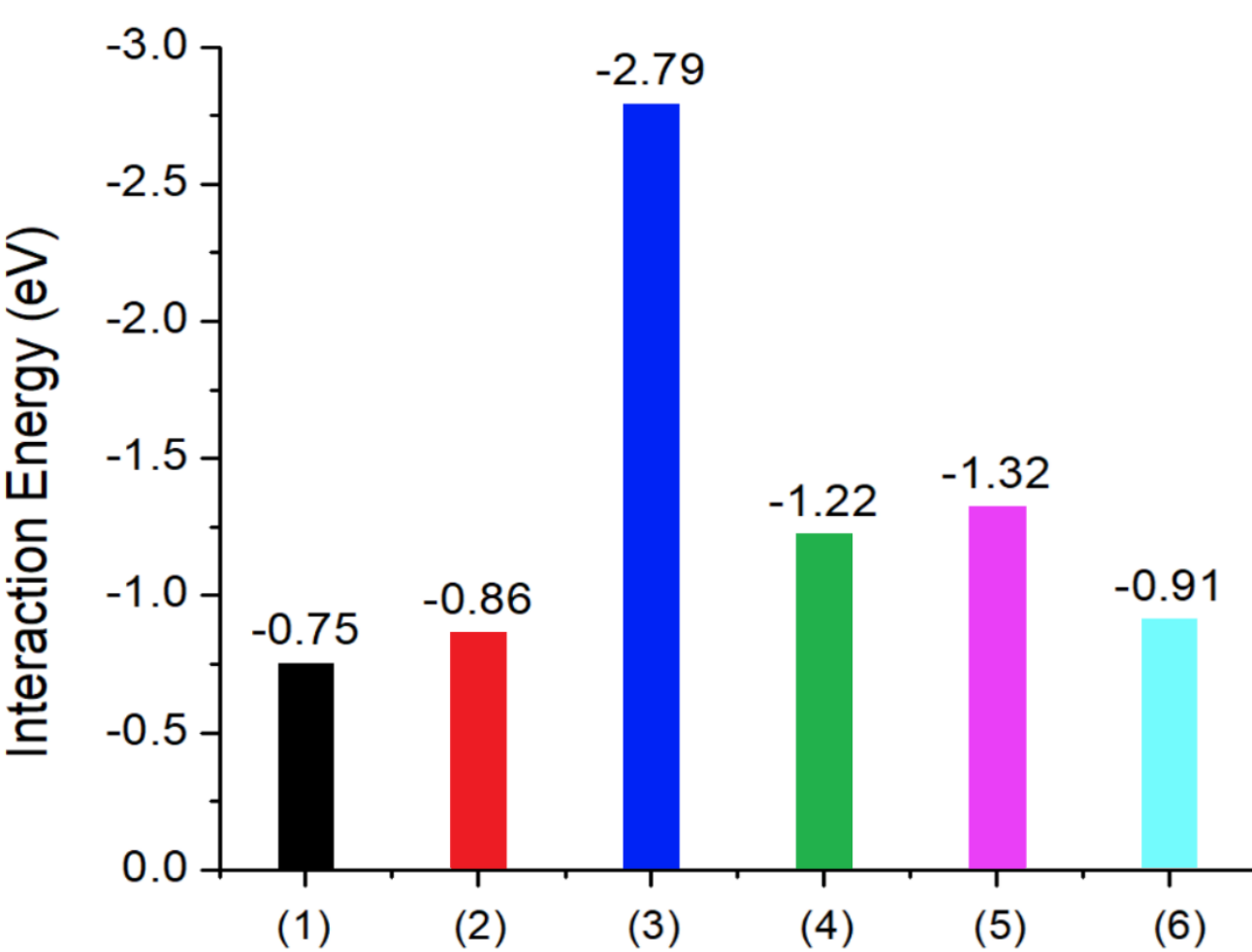


Figure 6. CO₂ adsorption energies (eV) calculated on the (100) surfaces of the six investigated catalysts: (1) CeZrO (100), (2) LCPGY (100), (3) dp-LCPGY (100), (4) pyr-CeZrO (100), (5) part. ox. pyr-LCPGY (100), and (6) κ -CeZrO (100).

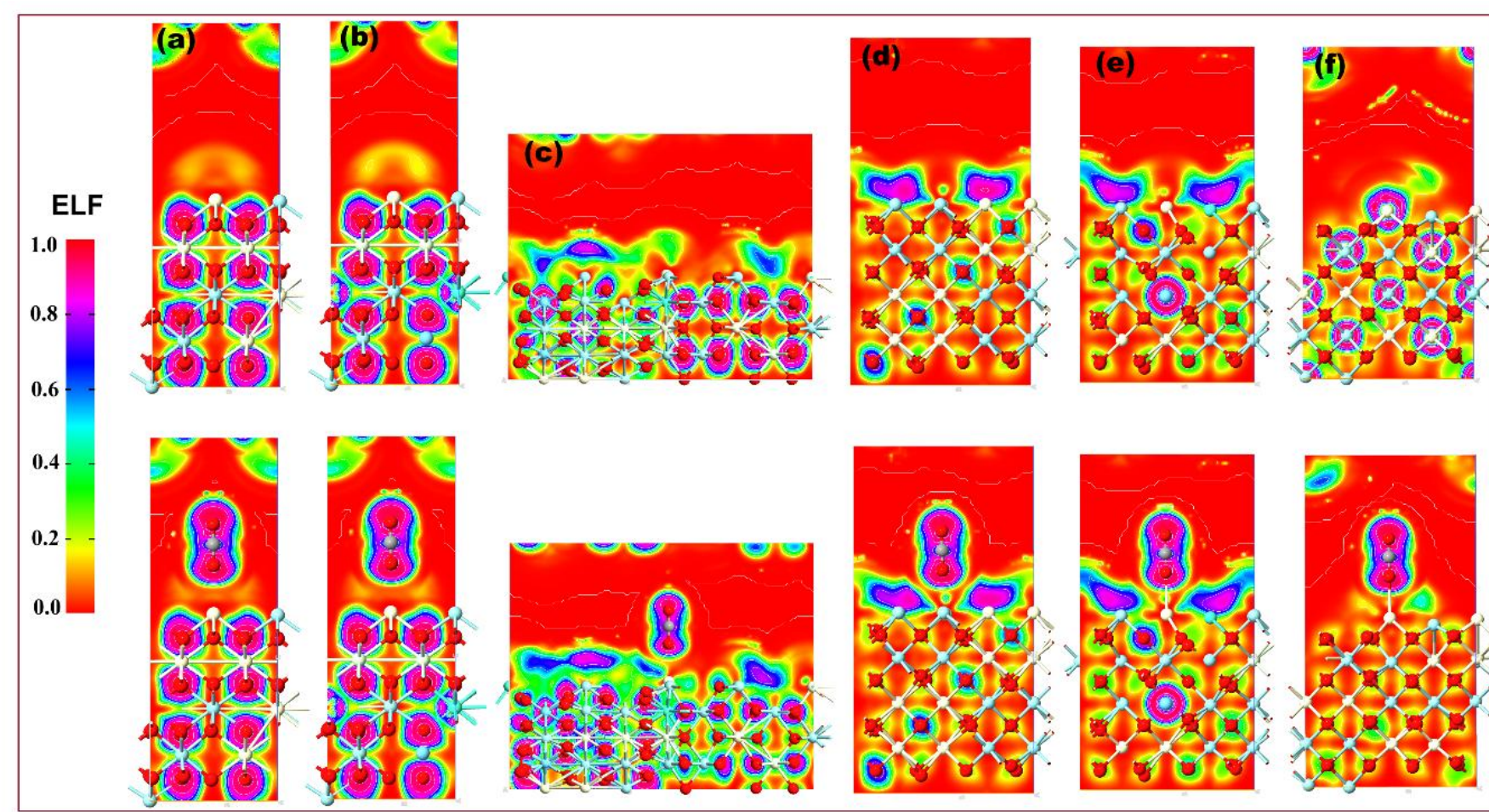


Figure 7. Electron localization function (ELF) maps of (a) CeZrO, (b) LCPGY, (c) dp-LCPGY, (d) pyr-CeZrO, (e) part. ox. pyr-LCPGY, and (f) κ -CeZrO. The top panels show clean surfaces, while the bottom panels correspond to CO₂ adsorbed configurations, respectively.

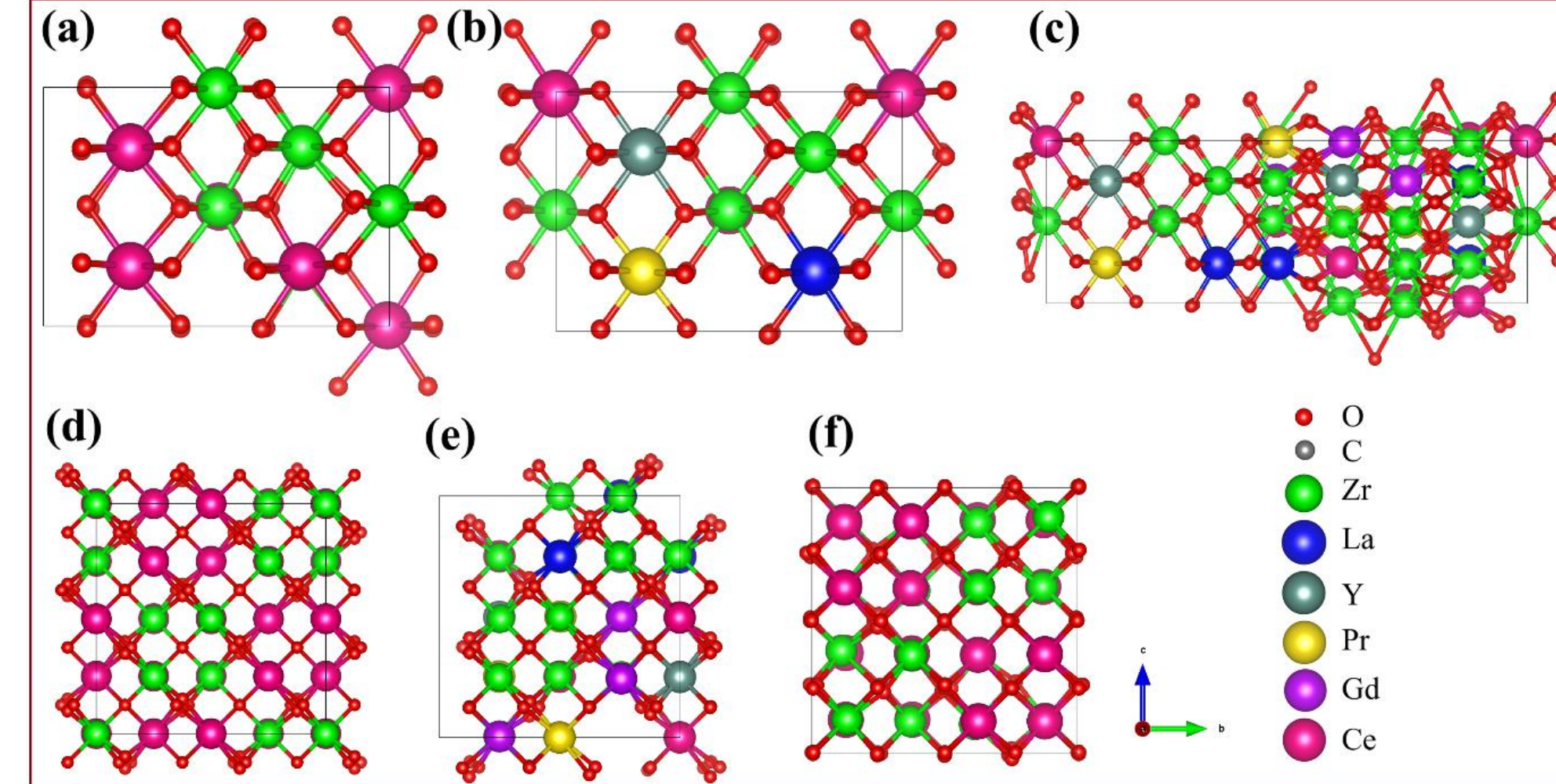


Figure 8. Optimized surface slab models of (a) CeZrO (100), (b) LCPGY (100), (c) dp-LCPGY (100), (d) pyr-CeZrO (100), (e) part. ox. pyr-LCPGY (100), and (f) κ -CeZrO (100) used in this study. Atom colors denote different elements as indicated in the legend.

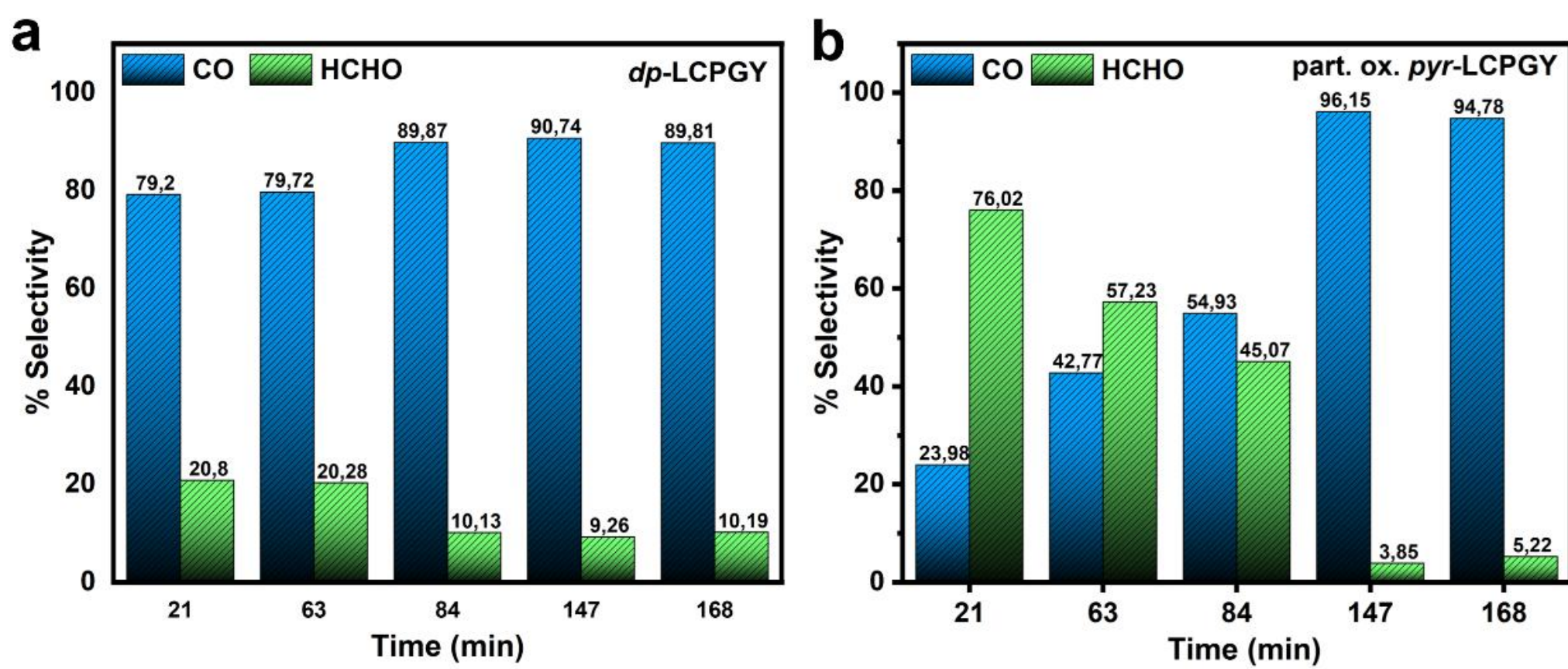


Figure 9. Selectivity values (%) for (a) dp-LCPGY and (b) part. ox. pyr-LCPGY during 168 minutes of reaction time for CO and HCHO, respectively.

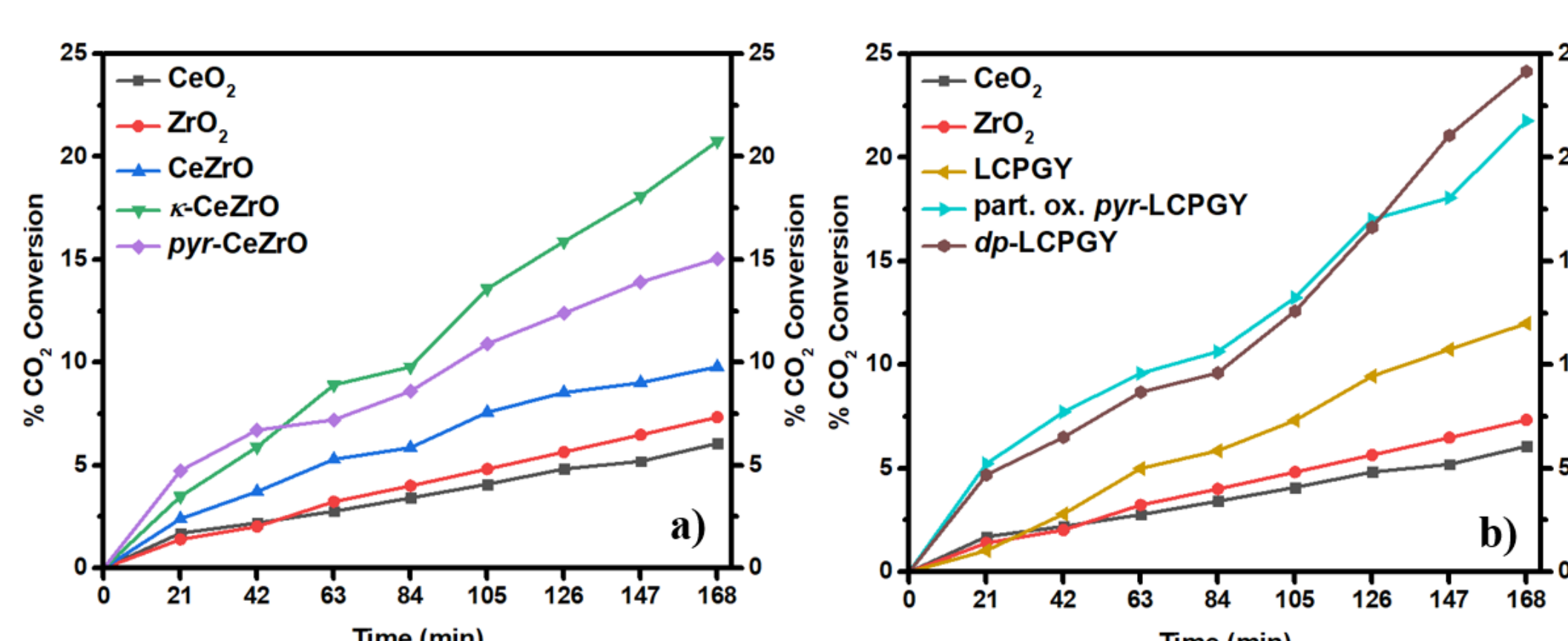


Figure 10. Catalytic conversion of CO₂ (%) during 168 minutes for a) CeZrO- and b) LCPGY-based materials.

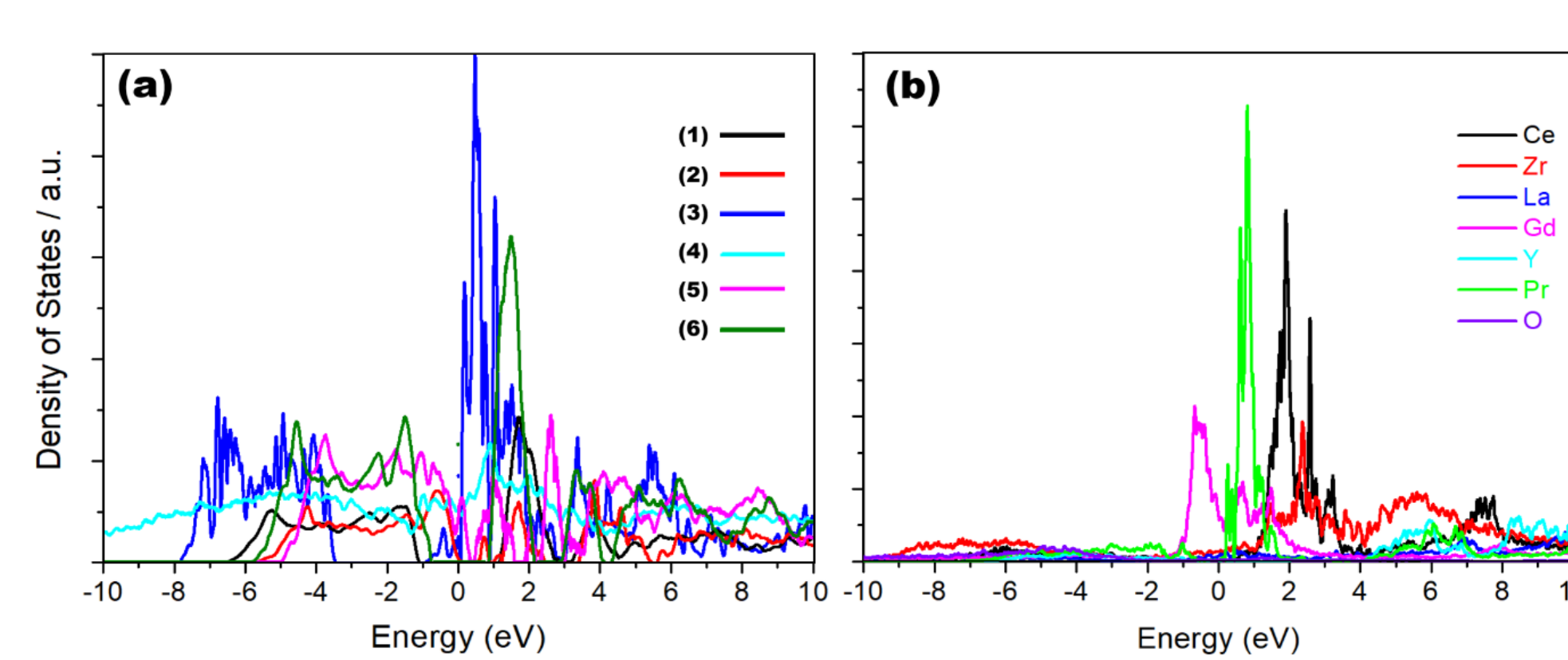


Figure 11. Total density of states (DOS) of (a) (1) CeZrO, (2) LCPGY, (3) dp-LCPGY, (4) pyr-CeZrO, (5) part. ox. pyr-LCPGY, and (6) κ -CeZrO. (b) Comparative PDOS plots of dp-LCPGY. The Fermi level is set to 0 eV.

CONCLUSIONS

A series of ordered, disordered, and high-entropy ceria-zirconia-based catalysts was successfully synthesized using an optimized sol-gel approach, yielding solid-solution, pyrochlore, κ -type, and partially oxidized phases. Visible-light-driven CO₂ hydrogenation showed the highest CO₂ conversion for dp-LCPGY (24.15%), followed by partially oxidized pyr-LCPGY (21.77%) and κ -CeZrO (20.75%). High-entropy pyrochlores additionally enabled HCHO formation, indicating enhanced multielectron reduction pathways. DRIFTS and DFT analyses revealed that oxygen vacancies and Ce/Pr redox centers promote CO₂ adsorption and activation, with Ce sites adjacent to oxygen vacancies identified as particularly favorable. The strong CO₂ adsorption of dp-LCPGY correlated with its superior photocatalytic performance. Overall, defect-engineered high-entropy ceria-zirconia oxides show promising potential for visible-light CO₂ conversion and provide a basis for the rational design of advanced photocatalysts.

REFERENCES

- ¹Tatar D. et. al., ACS Appl. Mater. Interfaces, **2024**, 16, 29946-29962.
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