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Dye degradation via the photocatalytic activity of single perovskites

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INTRODUCTION

Perovskites are materials that have the same crystal structure as the first mineral found with that structure, calcium titanium oxide ($CaTiO_3$). Perovskite compounds have a chemical formula ABX_3 where 'A' are cations with larger radii, 'B' are cations with smaller radii, and 'X' are anions that bond to both 'A' and 'B'. This research aimed to synthesize high-entropy perovskites via the modified citrate sol-gel method which can be used in dye degradation. The starting perovskite material $CeNiO_3$ was characterized by powder X-ray diffraction and Brunauer-Emmet-Teller surface area analysis to prove phase purity and pore size/specific surface. Since perovskites possess high catalytic activity, synthesized materials were tested by UV/Vis spectroscopy in 2 mL quartz cuvettes and a 20W halogen lamp. The photocatalytic activity of the $CeNiO_3$ and its high entropy forms were tested on the degradation of synthetic dyes: methylene blue (MB), naphthol green B (NG), and rhodamine B (RDB) respectively. The results indicate a reduction of maximum absorbance of tested dyes in the given time frame and monitored during irradiation at the wavelength of maximum absorbance for each dye (663 nm for MB, 734 nm for NG, and 554 nm for RDB).

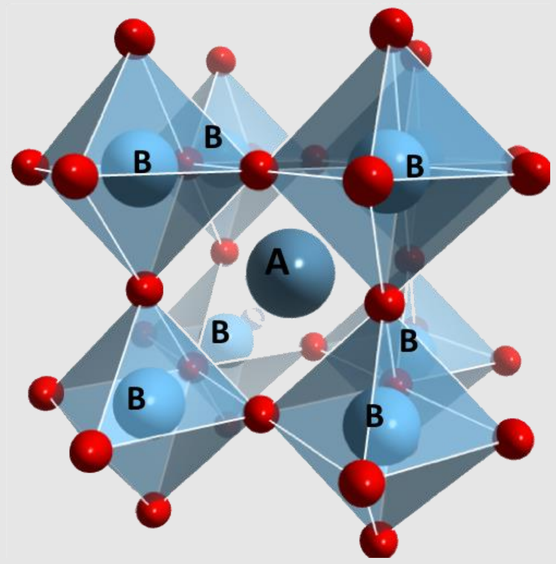

Fig.1. General perovskite structure.

SYNTHESIS

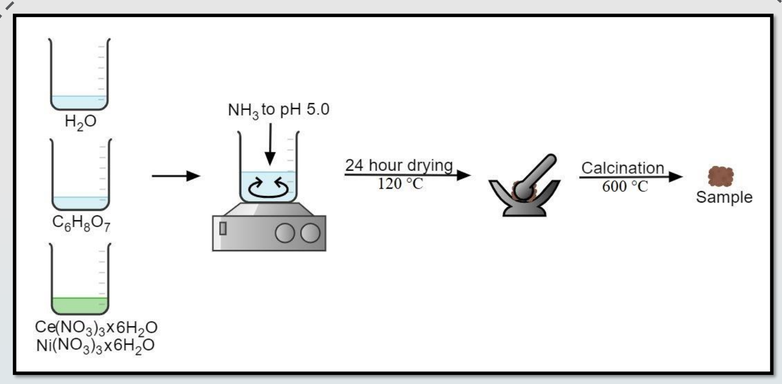

Fig 2. Synthesis pathway for obtaining phase-pure HEOs.

Table 1. Chemical formulae with configuration entropy value for each compound.

Code	Chemical formula	S_{config}
RB1	$CeNiO_3$	0
RB11	$CeNi_{0.25}Cu_{0.25}Mg_{0.25}Zn_{0.25}O_3$	1.386
RB31	$Ce_{0.2}La_{0.2}Pr_{0.2}Sm_{0.2}Eu_{0.2}NiO_3$	1.609

Table 2. Estimated indirect and direct band gap values for each compound from absorbance spectra via the Tauc method.

Band gap		
Sample	Direct	Indirect
RB1	5.69	5.16
RB11	5.61	5.18
RB31	5.74	5.21

RESULTS

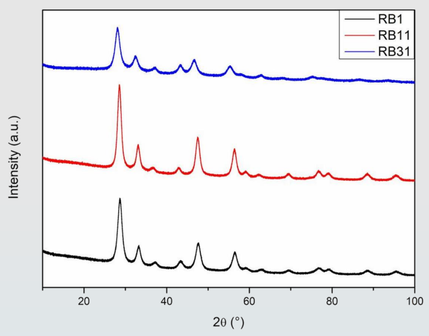

Fig.3. Powder X-ray diffraction patterns (PXRD) of RB1, RB11, and RB31 recorded before thermogravimetric analysis. Given PXRD patterns indicate phase purity of synthesized compounds.

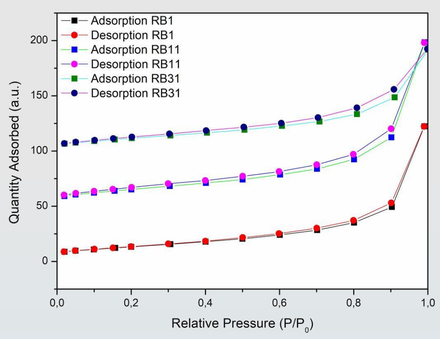

Fig.4. BET isotherms of RB1, RB11, and RB31 analyzed using the multi-point BET method.

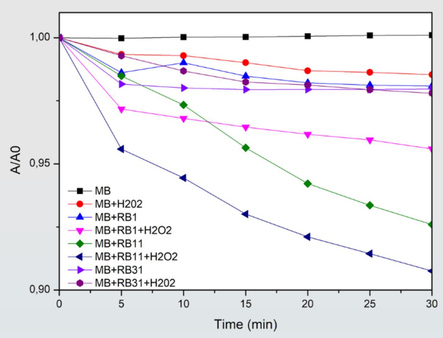

Fig.5. UV-Vis absorption spectra of methylene blue (MB) dye with and without the addition of HEOs monitored at regular intervals of time under halogen lamp (20 W) irradiation at λ = 663 nm.

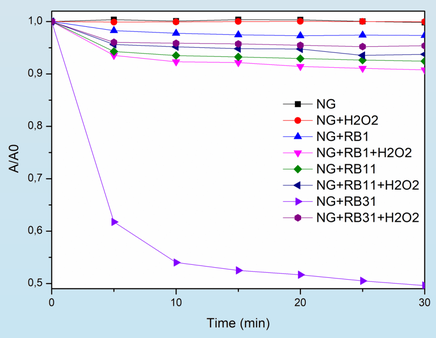

Fig.6. UV-Vis absorption spectra of naphtol green (NG) dye with and without the addition of HEOs monitored at regular intervals of time under halogen lamp (20 W) irradiation at λ = 734 nm.

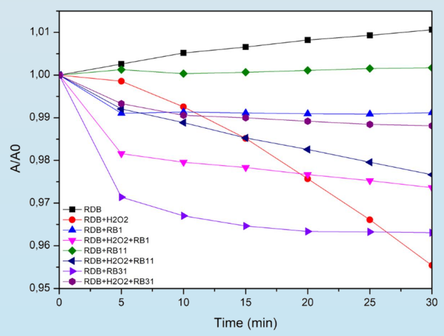

Fig.7. UV-Vis absorption spectra of rhodamine B (RDB) dye with and without the addition of HEOs monitored at regular intervals of time under halogen lamp (20 W) irradiation at λ = 554nm.

Table 3. Pore volume and specific surface area values for each compund obtained by DFT and multi-point BET methods.

Sample	Pore volume cc/g	Specific surface area m^2/g (DFT)	Specific surface area m^2/g (multi-point BET)
RB1	0,179	45,211	12,192
RB11	0,216	54,592	14,026
RB31	0,071	37,014	-

CONCLUSION

With the above green sol-gel method, phase-pure perovskites were synthesized which was proven by the powder X-ray diffraction analysis. RB1 is more efficient with the addition of hydrogen peroxide as an initiator and co-catalyst. RB11 was the most efficient in MB degradation (9 %), while RB31 was the most efficient for NG (50%) degradation after 30 minutes. Band gap results show that the above-mentioned materials belong to semiconducting materials which could be transformed to have insulating properties by adjusting the calcination temperature in the synthesis pathway.