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Photocatalytic activity of nanocrystalline $CeNiO_3$ perovskite and its entropy-stabilized derivatives towards azo dyes degradation

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INTRODUCTION

The need for new materials with a wide variety of properties has increased in the past few decades. For this reason, perovskite materials have been widely investigated due to the multiple possibilities of doping these compounds and tailoring their properties. Perovskites have been proven to be excellent candidates for a large number of new technologies. In this research, nanocrystalline oxide perovskites based on transition metals and lanthanides were synthesized. We introduced new elements by doping the parent structure, $CeNiO_3$, to increase the configurational entropy of the system. This approach has been used in order to increase their stability and induce new properties. 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. 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 using UV/Vis spectroscopy. 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).

SYNTHESIS

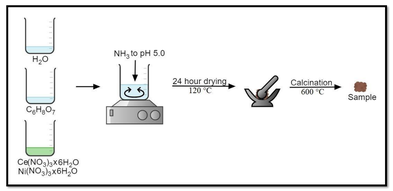

Fig 1. Synthesis pathway for obtaining phase-pure HEOs.

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

RESULTS

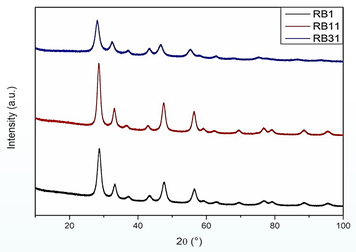

Fig.2. Powder X-ray diffraction patterns (PXRD) of RB1, RB11, and RB31. Given PXRD patterns indicate phase purity of synthesized compounds.

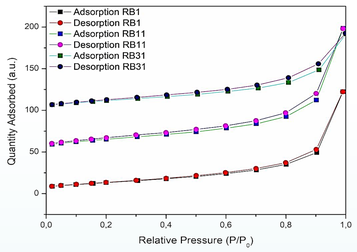

Fig.3. Physisorption N_2 isotherms of RB1, RB11, and RB31.

Table 2. Estimated indirect and direct band gap values for each compound from absorbance spectra via the Tauc method, together with physisorption properties of the compounds.

Sample	Band gap		Pore volume cm^3/g	Specific surface area m^2/g
	Direct	*Indirect*		
RB1	5.69	5.16	0,179	45,211
RB11	5.61	5.18	0,216	54,592
RB31	5.74	5.21	0,071	37,014

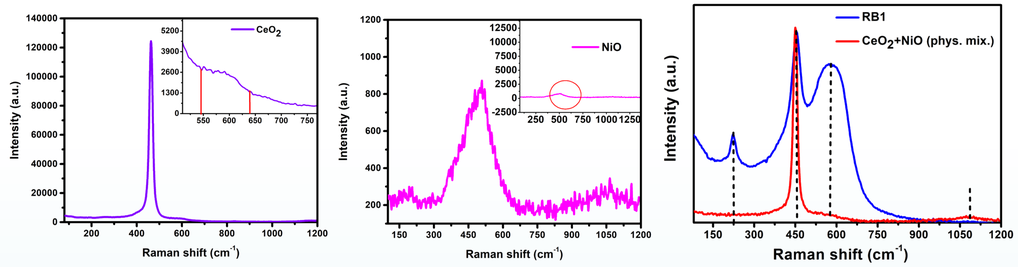

Fig.4. Raman spectrum of CeO_2 (left), NiO (middle), and overlapped Raman spectra of RB1 sample and physical mixture of cerium(IV) and nickel(II) oxide (1:1) (right).

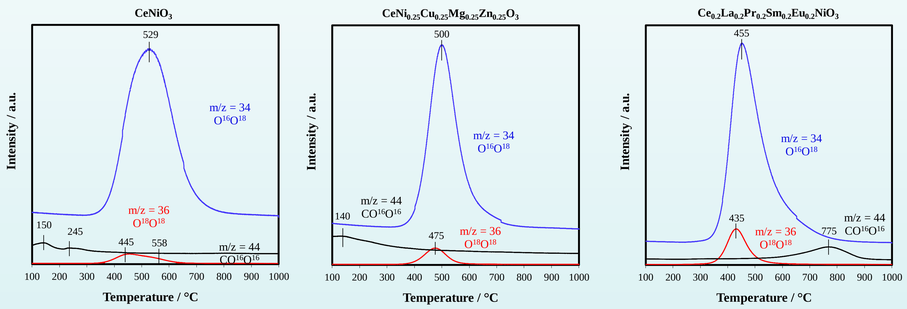

Fig.5. Oxygen exchange was monitored for all compounds using TG/MS method. It appears that oxygen surface exchange is enhanced with higher entropy on Ni position and even more with high entropy on Ce position.

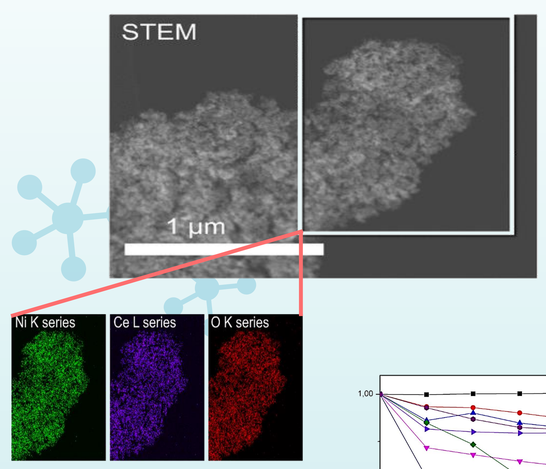

Fig.6. STEM-EDS mapping of RB1 ($CeNiO_3$) nanoparticles agglomerate.

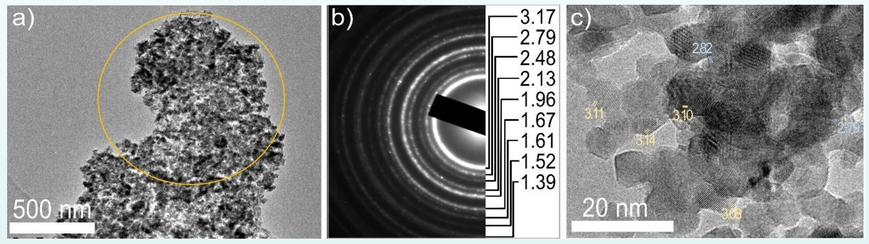

Fig.7. a) TEM image of RB1 ($CeNiO_3$) nanoparticle agglomerate and b) corresponding SAED with assigned d-values in Å; c) HRTEM of RB1 ($CeNiO_3$) nanoparticles, d-values in Å.

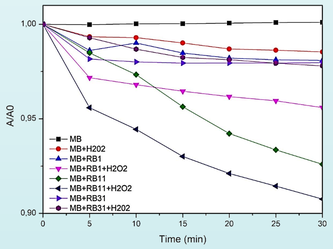

Fig.8. UV-Vis absorption spectra of methylene blue (MB) dye with and without the addition of HEOs monitored at regular intervals of time under halogen lamp (20 W) irradiation at λ = 663 nm.

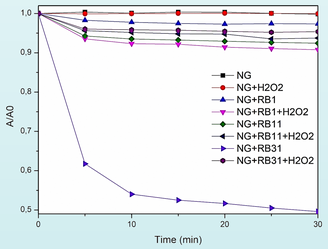

Fig.9. UV-Vis absorption spectra of naphtol green (NG) dye with and without the addition of HEOs monitored at regular intervals of time under halogen lamp (20 W) irradiation at λ = 734 nm.

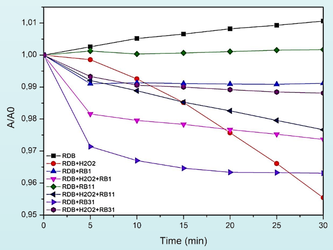

Fig.10. UV-Vis absorption spectra of rhodamine B (RDB) dye with and without the addition of HEOs monitored at regular intervals of time under halogen lamp (20 W) irradiation at λ = 554nm.

CONCLUSIONS

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. Raman spectroscopy was used to compare the vibrational modes of pure oxides, a physical mixture of oxides, and a compound RB1. The Raman results showed distinct differences between the pure oxides, the physical mixture, and the RB1 compound, indicating that the RB1 compound is a new and distinct compound that differs from both the pure oxides and the physical mixture.