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The effect of nanomaterial shape on formation of oxygen vacancies: non-doped and doped ceria

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INTRODUCTION

Oxygen storage in solid catalyst is very important for heterogeneous oxidation reactions of environmentally harmful gases such as CO, CH_x and HCl. Ceria nanoparticles act as promising catalysts these kind of reactions because it possesses high OSC (oxygen storage capacity). When reducing size of a material, surface becomes more important than a bulk. Also, surface defects are induced which favor high OSC. This is why in these kinds of reactions the interaction of a gas phase with solid surface is studied in detail. Redox reactions which occur on ceria surface usually follow Mars-van Krevelen mechanism (surface oxygen atoms directly involved in reactions). Neutral oxygen vacancies are formed because of the reversible change in oxidation state from Ce^{4+} to Ce^{3+}. These vacancies are formed in different quantities depending on a shape of synthesized nanomaterial. Different shapes show different facets of preferential orientation ((110) for nanorods and (100) for nanocubes) thus also showing different stability and activity.

EXPERIMENTAL

1 mmol of $Ce(NO_3)_3 \cdot 6H_2O$ in 2.5 mL of distilled water

+

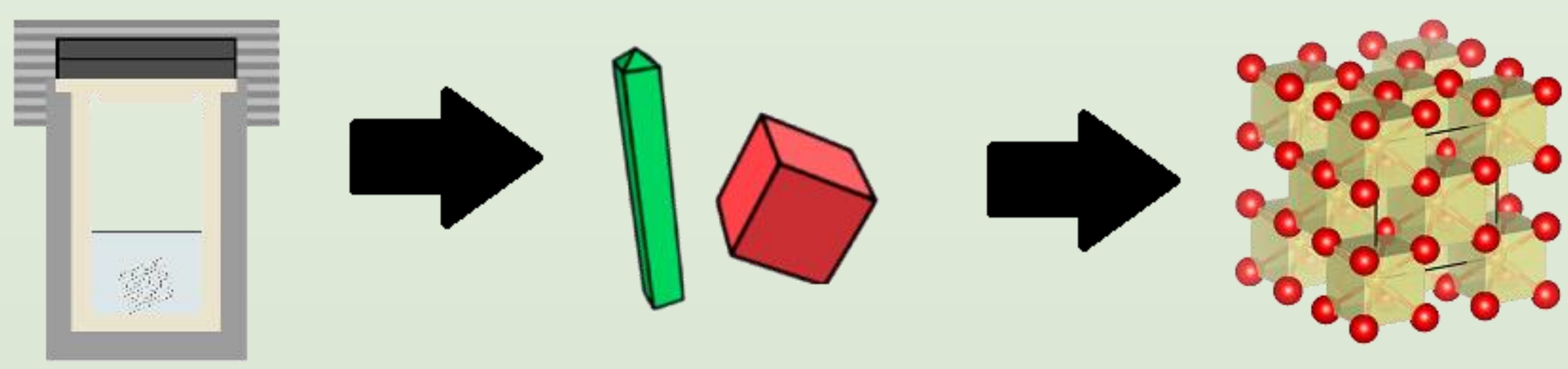
6M solution of NaOH (4.8 g in 17.5 mL of distilled water)

→

Hydrothermal synthesis in an autoclave for 24 h
- 100 °C for rods
- 180 °C for cubes

→

Calcination at 600 °C for 6 h



RESULTS AND DISCUSSION

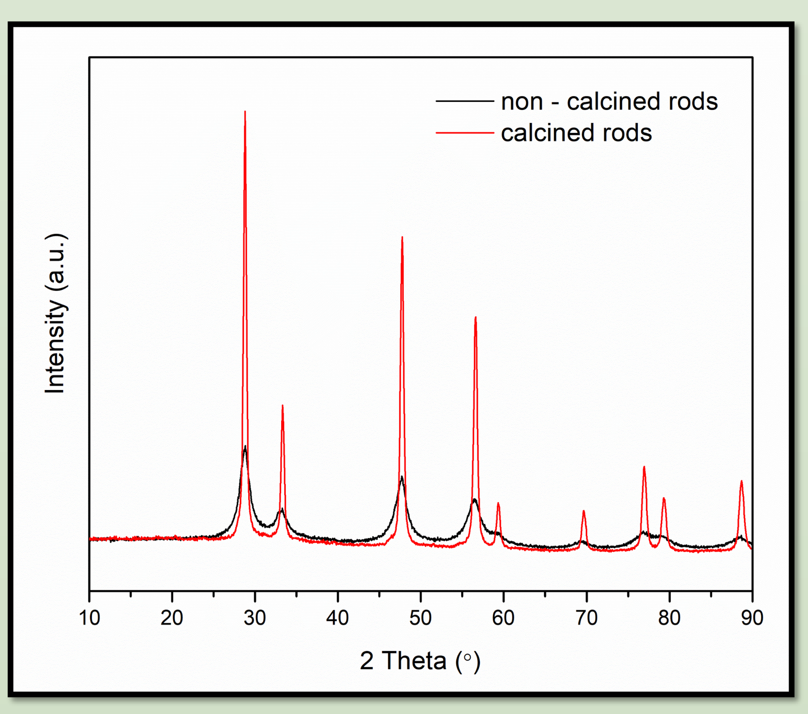


Figure 1. XRD of pure ceria nanorods before and after calcination. It is evident that calcination step is needed for formation of highly crystalline phase of ceria nanorods.

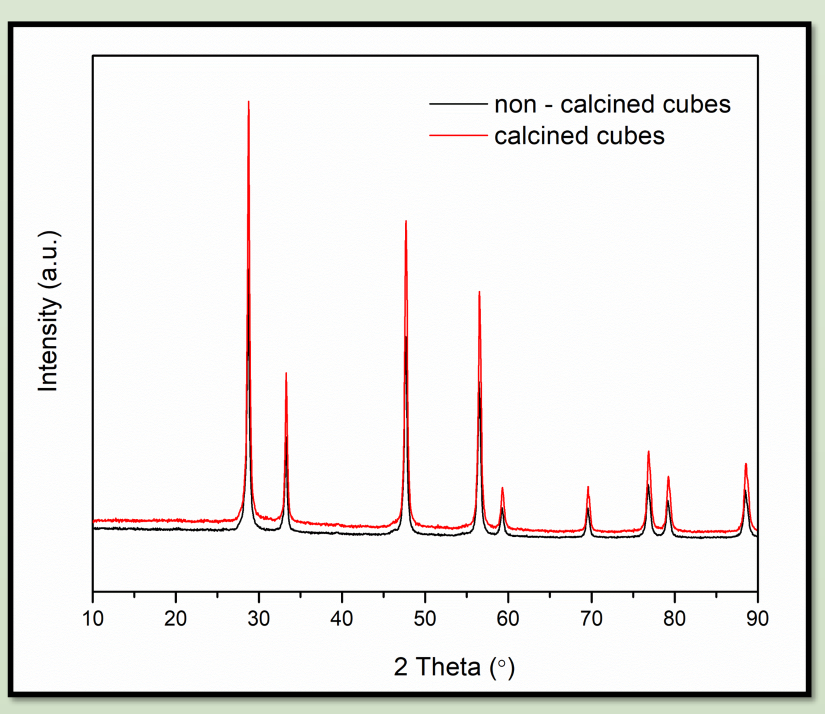


Figure 2. XRD of pure ceria nanocubes before and after calcination. It is evident that calcination step is needed for formation of highly crystalline phase of ceria nanocubes.

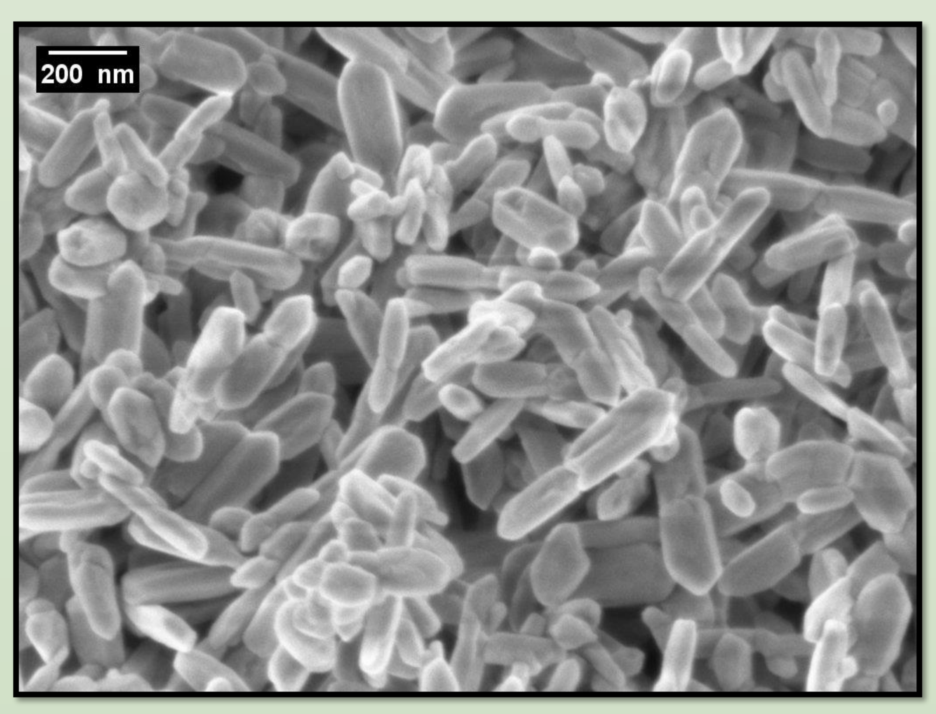


Figure 5. SEM image of synthesized nanorods. This morphology is obtained for both doped and non-doped ceria. Shape of nanorods is irregular and with different lengths and widths.

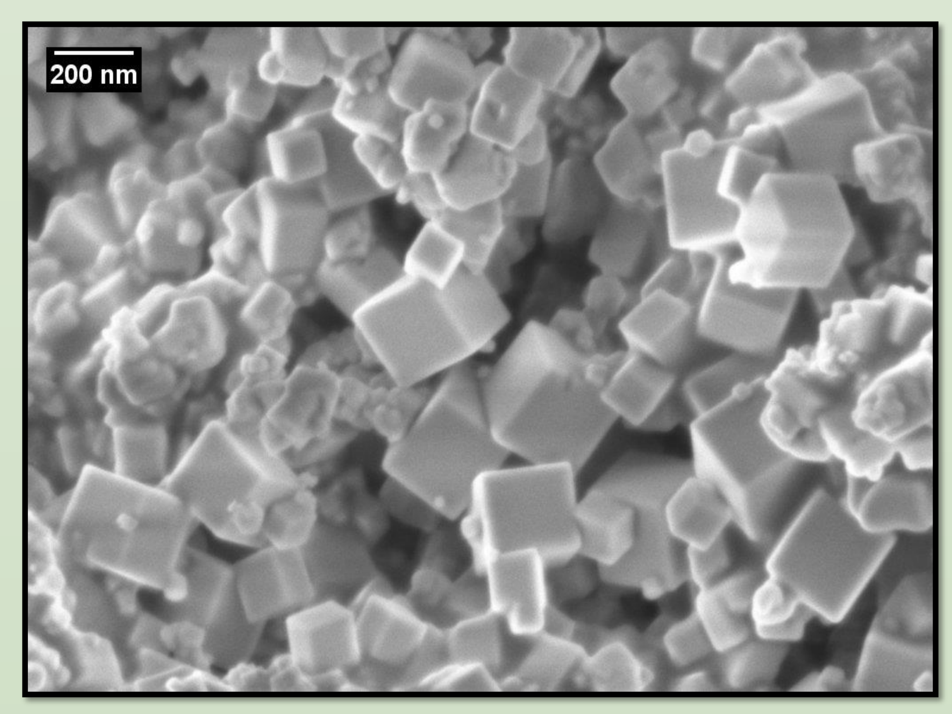


Figure 6. SEM image of synthesized nanocubes. This morphology is obtained for both doped and non-doped ceria. Shape of nanocubes is very regular, but the sizes of cubes are not uniform.

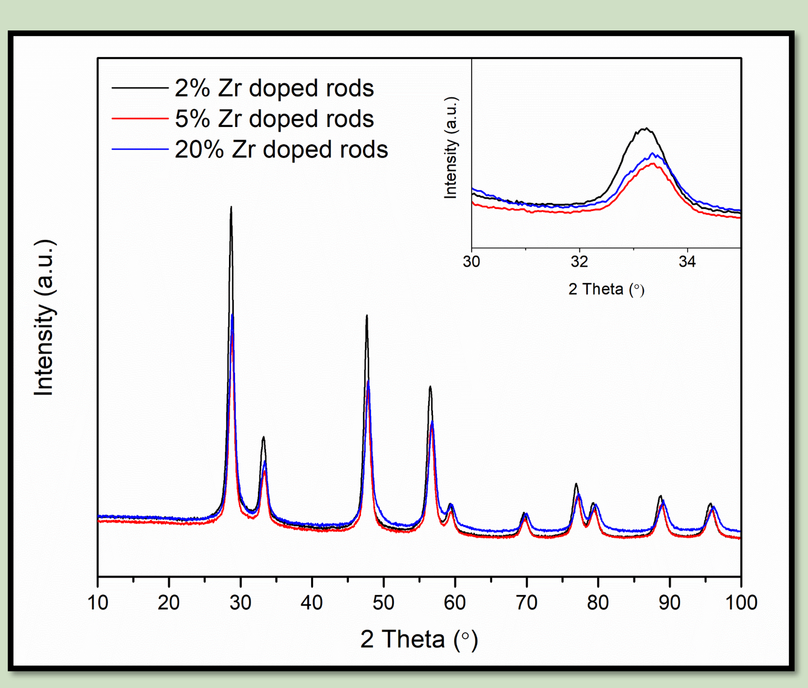


Figure 3. XRD of Zr-doped ceria nanorods. There is a slight shift around given 2θ positions which corresponds to different dopant concentrations and lattice distortions.

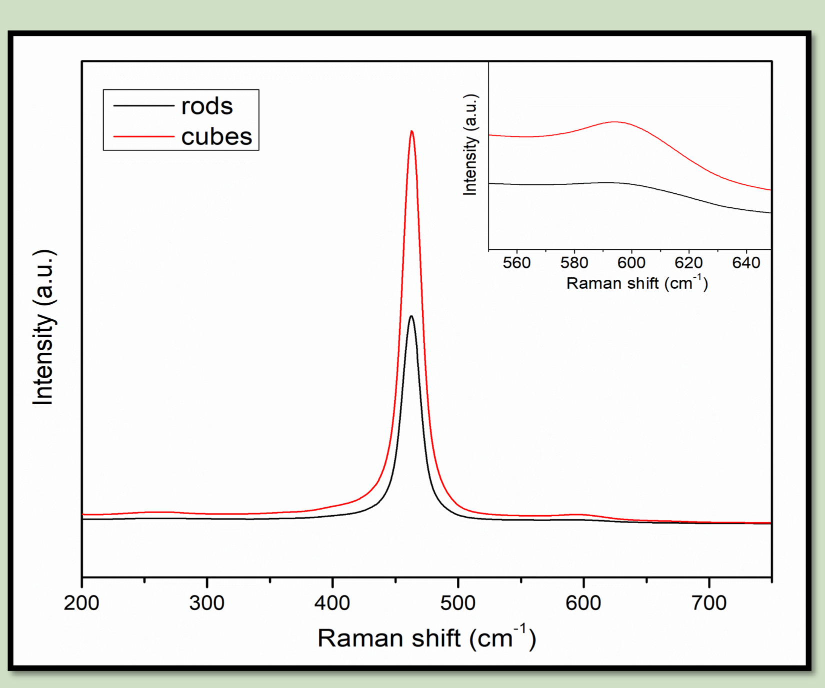


Figure 4. Raman spectra of ceria nanorods and nanocubes shows Raman active mode in the interval between 440-480 cm^{-1} and vacancy mode in the interval between 540-630 cm^{-1} in the inset.

Table 1. Oxygen vacancy concentration in pure ceria calculated from Raman spectra

Nanorods	11.41 %
Nanocubes	10.63 %

Ratio of intensity integrals of vacancy mode and Raman active mode is defined as oxygen vacancy concentration.

$$\boxed{O_O^X + 2Ce_{Ce}^X \rightarrow V_O^{\cdot\cdot} + 2Ce_{Ce}^{I} + \frac{1}{2}O_2(g)}$$

Kröger-Vink notation

Equation that describes formation of oxygen vacancies on the surface of ceria.
(**X** = no charge; **•** = positive charge; **I** = negative charge)

CONCLUSIONS

In this research, shape-controlled CeO_2 nanoparticles (nanorods and nanocubes) and Zr-doped ceria nanorods were synthesized by hydrothermal method. Synthesized materials have been characterized by powder X-ray diffraction (PXRD), Raman spectroscopy and scanning electron microscopy (SEM). Obtained results show pronounced effect of different nanoshape of ceria on formation of oxygen vacancies.