According to the recent studies, it is expected that the global energy requirement will increase from 14 TW to 30 TW by the year 2050. Currently, fossil fuels are the major energy source utilized for the fulfillment of the energy requirement. Due to the excessive utilization of fossil fuels, the concentration of greenhouse gases in the atmosphere is increasing day by day and hence there is a pressing need to develop technologies to produce carbon free renewable fuels. The liberated CO$_2$ can be re-energized into CO via ferrite based thermochemical looping process using concentrated solar energy. The CO produced via solar thermochemical CO$_2$-splitting can be combined with H$_2$ derived from ferrite based solar thermochemical water-splitting process to produce solar syngas which can be further processed to liquid fuels such as Methanol, Diesel, and Kerosene via the Fischer-Tropsch process. The current research trends in solar thermochemical community are focused towards high and constant levels of solar fuel production in multiple cycles and it is believed that non-volatile mixed metal oxides such as undoped and doped ceria will significantly improve the production of solar fuels. Ceria based redox cycle comprises of two steps. First step belongs to solar endothermic reduction of ceria at higher temperatures releasing O$_2$. The second step corresponds to the non-solar exothermic re-oxidation of the reduced ceria at lower temperatures by H$_2$O, CO$_2$, or a mixture of the two producing H$_2$, CO or syngas.

In this investigation, Zr and Hf doped ceria based redox nanoparticles (various doping combinations) were synthesized using a co-precipitation method. The respective metal precursors were dissolved in water. Upon complete dissolution, excess ammonium hydroxide (NH$_4$OH) was added drop-wise to the mixture under vigorous stirring to precipitate the mixed-metal hydroxides (final pH = ~9). The obtained precipitates were filtered, washed with water until free
from anion impurities and oven dried at 100 °C for 8–10 h. Subsequently calcination was performed at different temperatures in air. The calcined powders were characterized by powder X-ray diffraction, BET surface area analysis, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The compositional purity of the derived Zr/Hf doped ceria was identified using powder XRD and the obtained results indicate phase pure composition of the derived materials (based on the stoichiometry selected during synthesis). The derived Zr/Hf doped ceria also possess high specific surface area (SSA) and porosity which is confirmed by BET analysis. The SEM and TEM analysis indicate formation of Zr/Hf doped ceria nanoparticles in the range of 10 to 50 nm. Synthesized Zr/Hf doped ceria nanoparticles were further tested for thermochemical CO₂-splitting by using a high-temperature thermogravimetric analyzer (TGA). Multiple thermal reduction and oxidation (by CO₂) cycles were performed at various operating conditions by using TGA while the O₂ and CO was quantified by gas chromatography. Results obtained indicate that the derived Zr/Hf doped ceria is capable of producing higher amounts of solar CO as compared to previously investigated undoped and doped ceria materials. Also, the Zr/Hf doped ceria was examined in 20 thermochemical cycles towards successive thermal reduction and CO₂ splitting reactions and the obtained findings indicate stable redox reactivity and thermal stability.