Acetate-assisted synthesis of ceria nanoparticles

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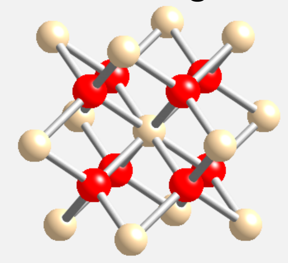
Background

Nanostructured cerium (IV) oxide (ceria) has unique catalytic properties because of its high surface area to volume ratio and greater amount of oxygen vacancy defects when compared to bulk ceria. There are several synthetic methods for producing ceria, but many are expensive, time-consuming, and involve dangerous reagents. We recently reported a rapid method to generate ceria nanoparticles through direct ozonation of cerium (III) nitrate in ethanol, but with only *ca.* 10+% yield.*



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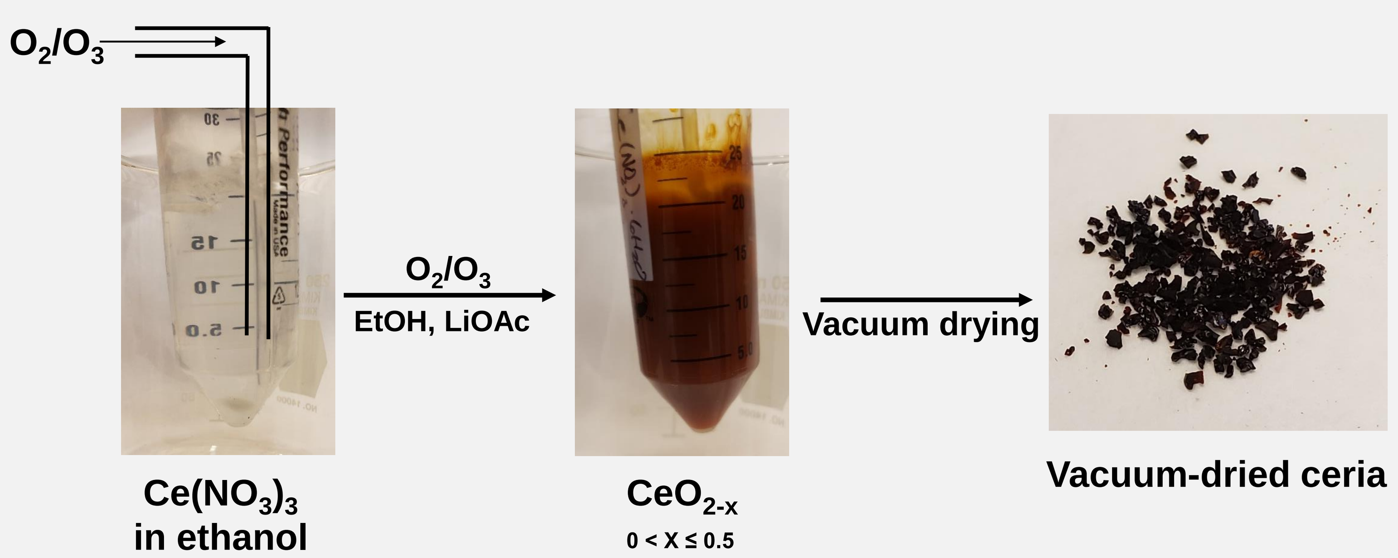
Objective

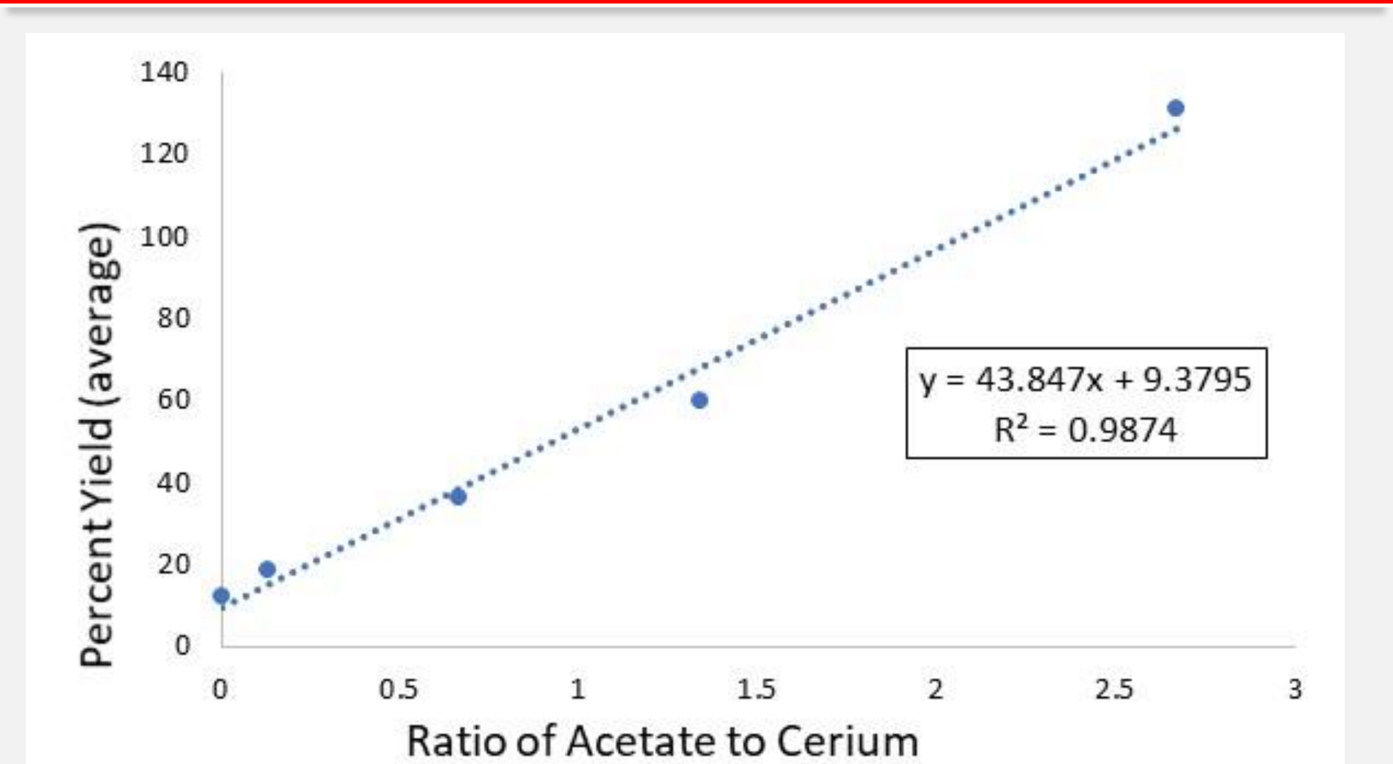
The main objective of this project was to optimize the yield of ceria nanoparticles from the standard ozone-mediated synthesis by controlling the acidity of the reaction with acetate.

Synthetic Scheme

Previous studies suggest that significant amounts of acetic acid are produced during the synthesis as ethanol is oxidized by ozone. The resulting increase in acidity was believed to limit the growth of nanoparticles. In order to control the acidity of the reaction, acetate species were added to the reaction solution in varying quantities.



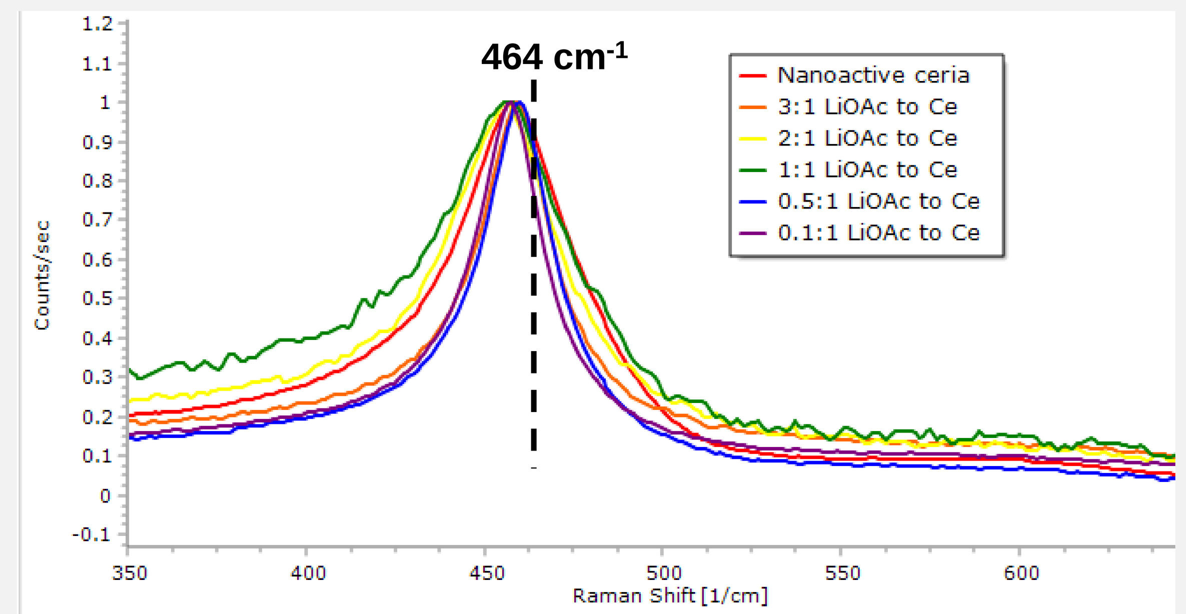
Yield Increase via Acetate Addition



The yield of ceria nanoparticles increased significantly at increasing molar ratios of lithium acetate (LiOAc) to cerium (III) nitrate ($Ce(NO_3)_3$), up to nearly 100% yield. Above a 2:1 LiOAc to $Ce(NO_3)_3$ ratio, the yield appears to increase above 100%. This suggests that with high amounts of LiOAc, side products such as cerium (III) acetate begin to form.

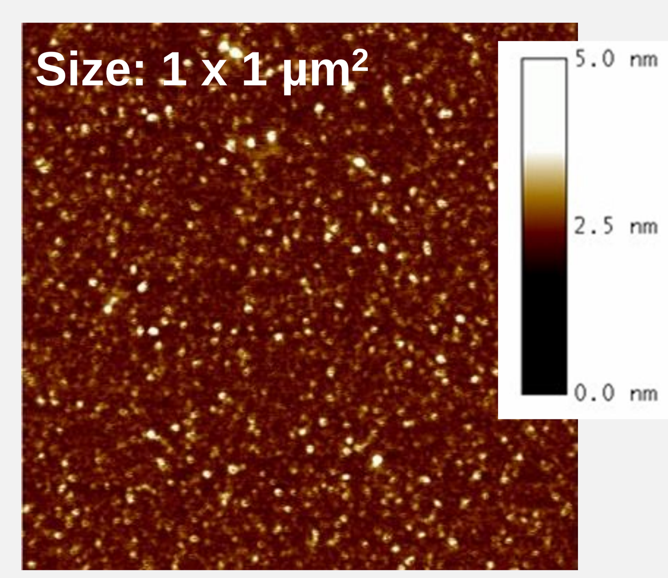
Characterization

Raman Spectra

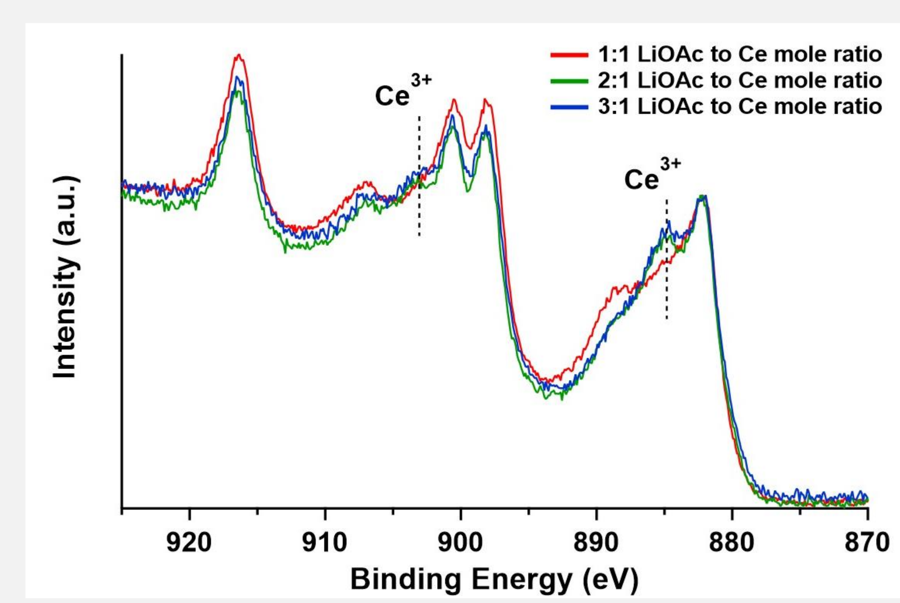


The F_{2g} mode of bulk ceria can be found around 464 cm^{-1}. Locations of Raman peaks of ceria products from the acetate-buffered syntheses are red-shifted, indicating that they are nanosized particles.

Atomic Force Microscopy



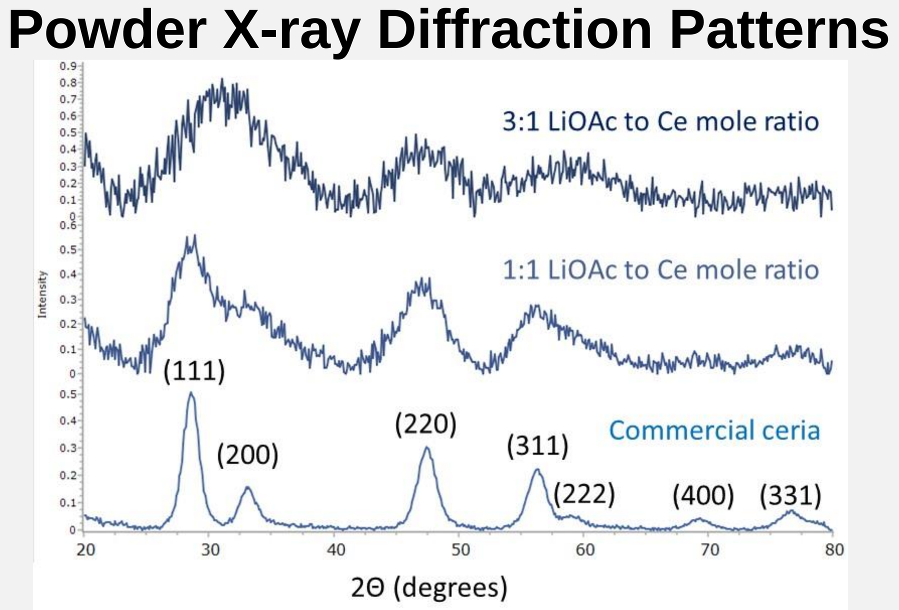
X-ray Photoelectron Spectra



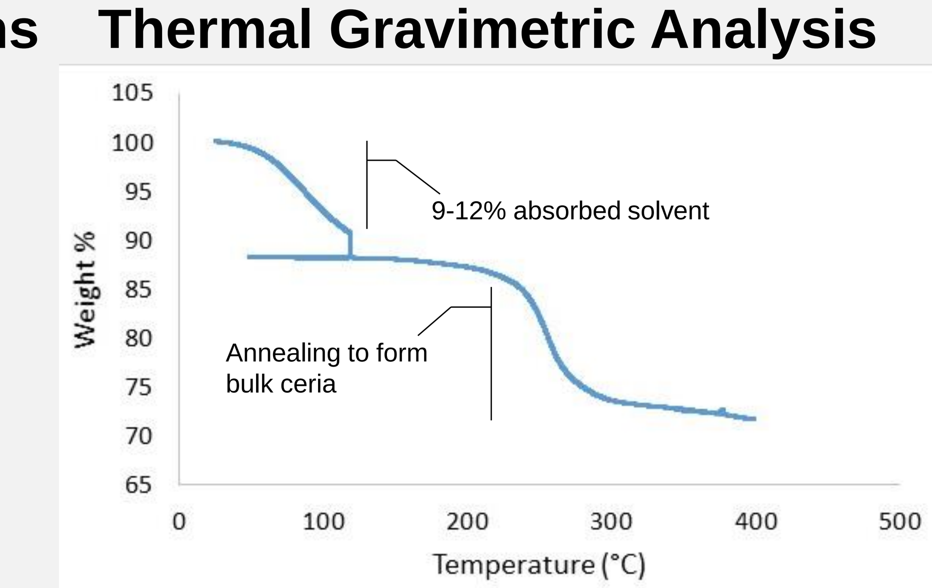
Atomic Force microscopy: Particle size typically ranges from 2-5 nanometers, on par with those observed in the standard ozone-mediated synthesis.

X-ray photoelectron spectra: With increasing mole ratios of LiOAc to $Ce(NO_3)_3$, there is an increase in the concentration of Ce^{3+} on the surface of ceria products. As a result, the density of oxygen vacancy defects is increased.

Powder X-ray Diffraction Patterns



Thermal Gravimetric Analysis



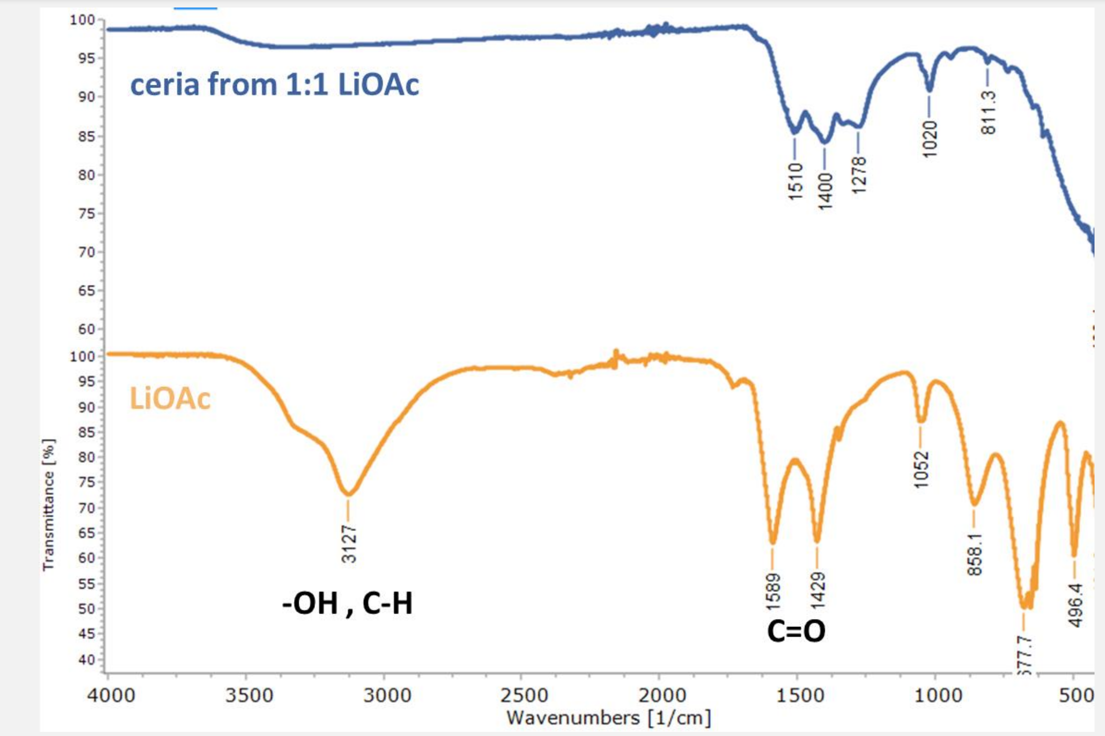
Powder X-ray diffraction patterns: Ceria particles synthesized with varying ratios of LiOAc to $Ce(NO_3)_3$ display diffraction peaks congruent with those of commercial ceria.

- Increasing the ratios of LiOAc to $Ce(NO_3)_3$ led to broadening of the diffraction peaks, suggesting a decrease in particle size or crystallinity.

Thermal gravimetric analysis: Residual solvent and organic byproducts are present among vacuum-dried ceria.

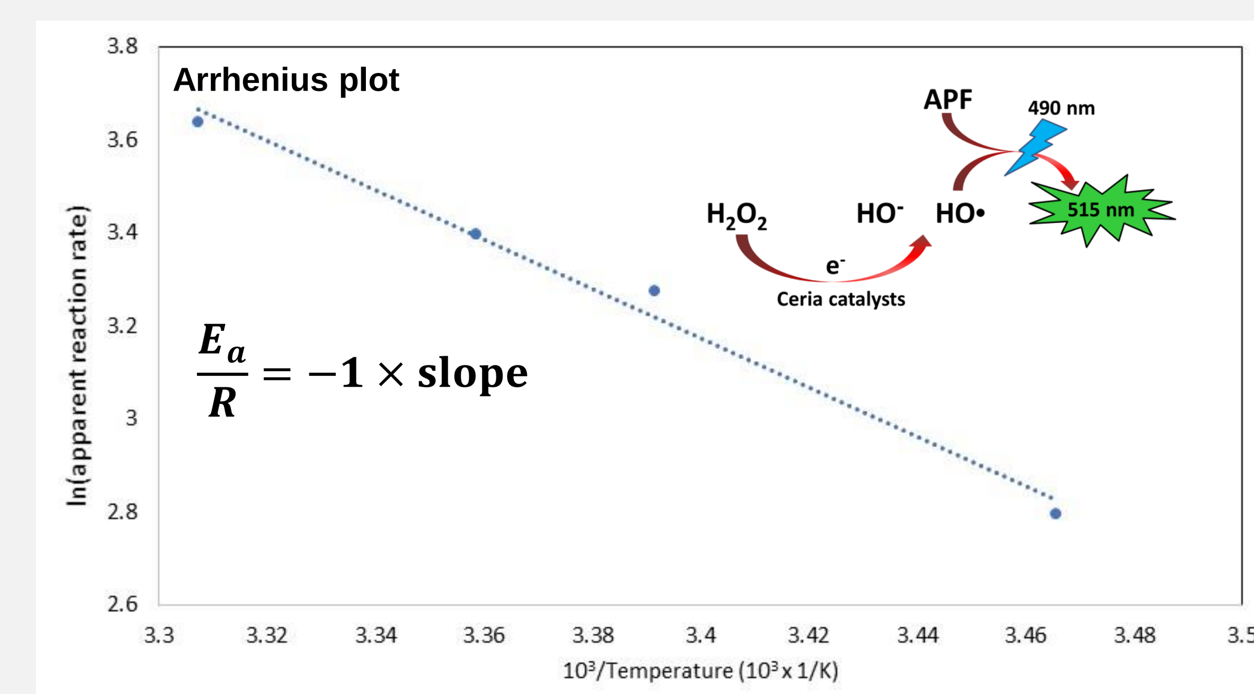
- Grinding the products and drying them in a convection oven at 120 °C for 1 h. successfully removed residual and byproducts, leading to *ca.* 9-12 % mass decrease.

Infrared Spectroscopy



While oven-drying removes most residual organic substances, it is suspected that carbonates may be bound to the surface of the ceria.

Generation of Hydroxyl Radicals



Activation energy, E_a (kJ/mol): 44 (nanoparticles) vs. 70 (bulk)

The decrease in crystallinity observed in the nanoparticles results in them having a greater number of catalytically active sites than bulk ceria.

Conclusion

- Adding lithium acetate increases the yield of the ozone-mediated synthesis of ceria nanoparticles from *ca.* 10 % to nearly 100 %.
- Size and crystallinity of ceria products decreases with increasing molar ratios of lithium acetate to cerium (III) nitrate.

Acknowledgments

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