2023

# Synthesis and Characterization of Pd/CeO2 Single Atom Catalyst for Oxygen Reduction Reaction

Samantha Ramesh
*Binghamton University--SUNY*

Prabhu Bharathan
*Binghamton University--SUNY*

# Synthesis and Characterization of Pd Single Atom Catalyst for Oxygen Reduction Reaction application

Konakanchi Gayatri Ramesh (Samantha)

Acknowledgement: Prabhu Bharathan; NSF support

Binghamton University, Binghamton, NY 13902

Fang Group

## Background

Single-Atom Catalysts (SACs) are a new frontier in heterogeneous catalysis, offering efficient utilization of precious metals[1].

Shape and size of Ceria nanocrystals are tunable and can be used as the support of SAC[2].

## Introduction

- Size and shape-controlled Ceria nanocrystals were synthesized using a two-phase solvothermal synthesis approach in the presence of oleic acid (for nanocubes) trioctylphosphine oxide (TOPO, for truncated nano-octahedra), and other organic species.
- Carbon-supported Pd on ceria nanocubes SAC ($Pd_1/CeO_2/C$) was prepared. It was compared with carbon-supported Pd on ceria nano-octahedral SAC.
- The Oxygen Reduction Reaction (ORR) characteristics of Pd-based SACs were studied.

## Chemicals Used

$Ce(NO_3)_3.6H_2O$, toluene, oleic acid, TOPO, tert-butylamine, ethanol, hexane, $PdCl_2$, Ketjen black carbon, 2-propanol, Nafion.

## Synthesis

- To synthesize $CeO_2$ nanocubes, $Ce(NO_3)_3.6H_2O$ as precursor, toluene, oleic-acid, tert-butylamine were mixed and transferred into a teflon-lined stainless-steel autoclave and heated at 180°C for 24 hours. The synthesis of $CeO_2$ truncated nano-octahedra was adopted from literature.[2]
- The products were separated using a separatory funnel, then washed with an ethanol/hexane mixture.
- Ceria nanocubes were mounted on carbon (loading of 40 wt%). Pd was then incorporated using $PdCl_2$ precursor followed by reduction using $NaBH_4$.
- Ink for electrochemical measurements was prepared by mixing $Pd_1/CeO_2/C$ with deionized (DI) water, 2-propanol, and Nafion.

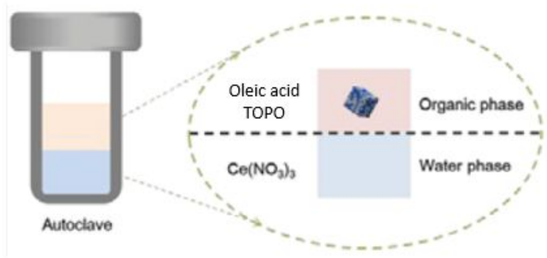



**Figure 1:** Two-phase solvothermal synthesis of Ceria.[2]

## Results

XRD analysis confirmed the formation of $CeO_2$ with characteristic diffraction peaks aligned with ICDD PDF card 34-0394.

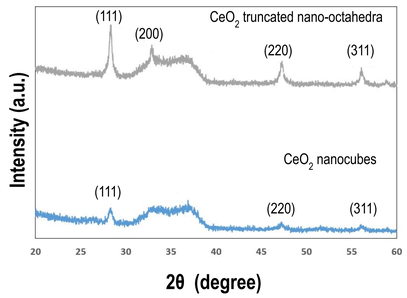



**Figure 2:** XRD patterns of $CeO_2$ nanocrystals.

Transmission electron microscopic (TEM) images confirm the morphologies of the synthesized $CeO_2$ nanocrystals, *i.e.*, the oleic acid-generated $CeO_2$ nanocubes and TOPO-derived $CeO_2$ truncated nano-octahedra.

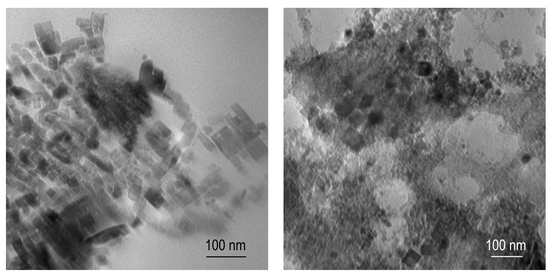
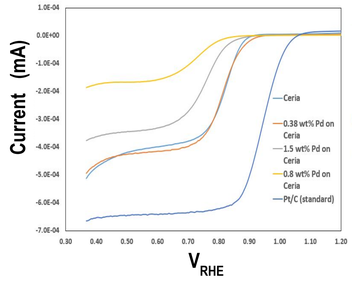



**Figure 3:** TEM images of oleic acid-developed ceria nanocubes (left) and TOPO-derived ceria truncated nano-octahedra (right).

ORR polarization curves of Pd loaded ceria showed catalytic activity. 0.38 wt% Pd loaded SAC showed the highest activity.




| Sample | Mass Activity of Pd ($A/g_{Pd}$) |
|---|---|
| Ceria | N/A |
| 0.38 wt% Pd on Ceria | 90.48 |
| 1.5 wt% Pd on Ceria | 3.56 |
| 0.8 wt% on Pd Ceria | 0.73 |
| Pt/C (standard) | N/A |

**Figure 4:** Voltammetry graph, showing the plot between current (mA) *vs* $V_{RHE}$ for various samples.

## Conclusions

- $Pd_1/CeO_2/C$ SACs were successfully prepared. They were also characterized using XRD, TEM, and electrochemical techniques.
- The $Pd_1/CeO_2/C$ SAC showed interesting catalytic activity towards the ORR.

## Future Work

- Investigate ORR characteristics by varying the Pd loading on $CeO_2$.
- Characterize $Pd_1/CeO_2/C$ SAC using Energy Dispersive X-ray Spectroscopy (EDX) to map the distribution of Pd on the substrate.

## References

1. Xiao-Feng Yang et al., ***Acc. Chem. Res.***, 46(8) 1740-1748 (2013).
2. Can Li et al., ***MRS Adv.***, 5(11) 523-529 (2020).