Synthesis and characterization of graphene quantum dot containing ceria-zirconia

Özgür Keleş[a], Andrew C. Dina[a,b], Daniel Fok[a]

[a]Chemical and Materials Engineering Department, San Jose State University, San Jose, CA

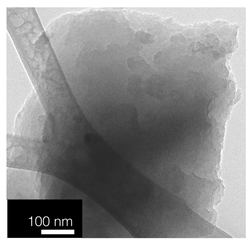
[b]Nanolab Technologies, 1708 McCarthy Blvd, Milpitas, CA 95035

Abstract: Zirconia-based nanoparticles are used in various applications, such as catalyst, filter, oxygen storage, and sensor. Among many synthesis methods to produce zirconia-based nanoparticles, aqueous sodium borohydride ($NaBH_4$) coprecipitation produces zirconia containing nano-pores [1]. In this work, we extended the $NaBH_4$ coprecipitation method to include ceria and graphene quantum dots (GQDs) in zirconia and characterized Ce-ZrO_2 and GQD-Ce-ZrO_2 nano-particles. These particles were calcined at 400 °C, 600 °C, and 700 °C to observe structural and phase changes. Aminated or carboxylated GQDs at 0.1 and 0.5 wt. % were added to the precursors to control nucleation sites for coprecipitation and to incorporate GQDs in zirconia. We performed SEM, TEM, XPS, XRD, and DSC characterization on calcined particles. SEM results showed agglomerated particles with clusters of few crystallites. DSC results were used to choose the calcination temperature and XRD results confirmed the tetragonal phase for calcinations >600 °C. Addition of ceria reduced the amorphous-to-tetragonal phase change temperature from 702 °C to 663 °C. XRD results showed that pure zirconia had ~19 nm crystal size; whereas, the ceria-zirconia had ~15 nm crystal size. TEM also supported the average crystal sizes found by the XRD. XPS compositional analysis showed that the Ce-ZrO_2 was synthesized to a stoichiometric composition of $Ce_{0.14}Zr_{0.86}O_2$. We observed agglomerated GQDs in the doped samples. Addition of GQDs changed the nano-porosity observed in zirconia via TEM. More studies are needed to elucidate nano-particle synthesis-structure relationships in the presence of GQDs.

Synthesis of GQD containing Ce-ZrO_2

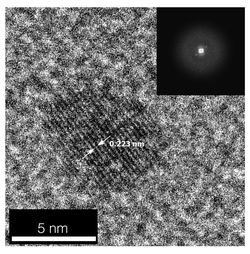
Produce GQDs from charcoal via oxidative cutting [2].

Charcoal



Acid
Heat
→
Filtration
Dialysis

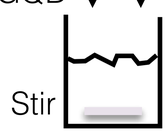
GQD



Produce ZrO_2 with or without Ce and GQDs via $NaBH_4$ reduction from [1].

$CeCl_3 \cdot 7H_2O$
$ZrOCl_2 \cdot 8H_2O$
w/ - w/o 0.5 wt. % GQD

5M $NaBH_4$
w/ - w/o 0.5 wt. % GQD

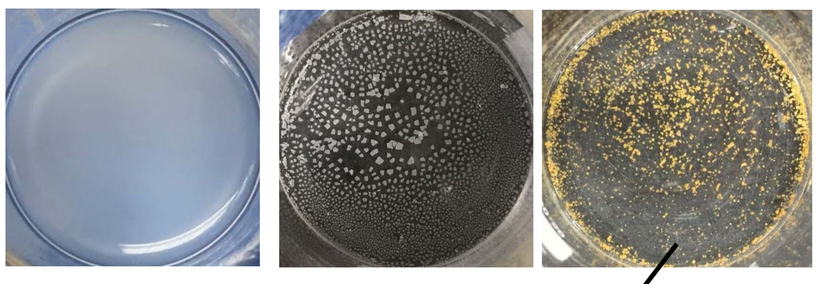


$$NaBH_4 + 4H_2O \rightarrow NaB(OH)_4 + 4H_2$$

$$4B(OH)_4 + Zr^{4+} + H_2 \rightarrow Zr(OH)_4 + 4B(OH)_3 + H_2$$

$$B(OH)_3 + 2H_2O \rightarrow B(OH)_4^- + H_3O^+$$

Wash
Dry
→
$Zr(OH)_4$
Ce-$Zr(OH)_4$
GQD-Ce-$Zr(OH)_4$
→
Calcination at 400 °C, 600 °C, and 700 °C

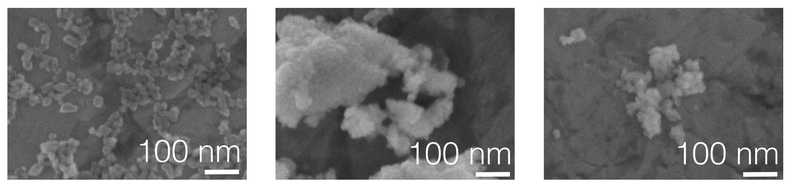


Obtain powders of
ZrO_2
$CeZrO_2$
CQD-$CeZrO_2$

Structure of ZrO_2, Ce-ZrO_2, and GQD-Ce-ZrO_2

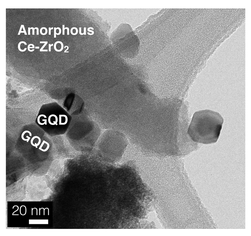
Zirconia powder morphology was not affected by the Ce and/or GQD additions.

ZrO_2 | $CeZrO_2$ | GQD-$CeZrO_2$



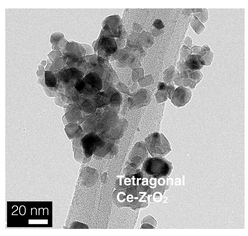
SEM images were taken at Nanolab Technologies (CA 95035) using an FEI Nova NanoSEM 430 equipped with a field emission electron gun operated at 5 kV.

Calcined at 400 °C

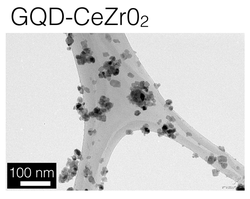


→ Amorphous Ce-doped zirconia crystallizes to tetragonal phase. GQDs burn at ~600 °C.

Calcined at 700 °C

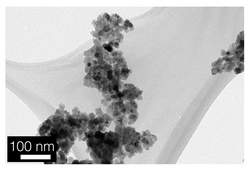


0.1 wt. % Aminated-GQD-$CeZr0_2$

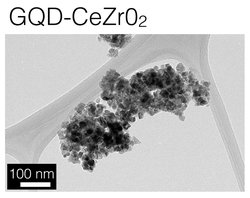


→ Change in functional groups of GQDs from amine to carboxyl affect calcined structure.

0.1 wt. % Carboxylated-GQD-$CeZr0_2$

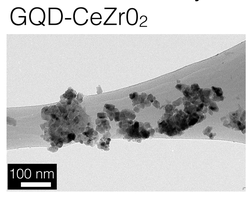


0.5 wt. % Aminated-GQD-$CeZr0_2$

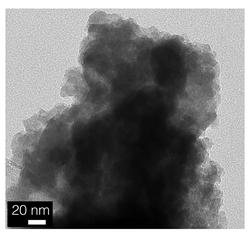


Increasing wt. % of GQDs resulted in more agglomerates, which might be due to the reduced H_2 bubbles as nucleation sites.

0.5 wt. % Carboxylated-GQD-$CeZr0_2$

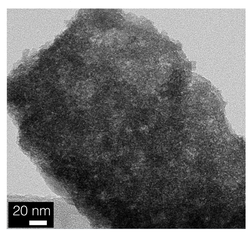


Amorphous ZrO_2



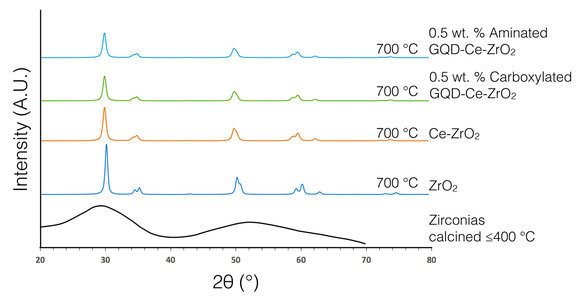
→ Addition of GQDs increased the porosity of amorphous zirconia.

Amorphous GQD-ZrO_2



TEM images were taken at Evans Analytical Group (CA 94086) using an FEI Tecnai TF-20 FEG/TEM at 200 kV or at Nanolab Technologies (CA 95035) using a JEOL JEM-2100 at 200 kV.

XRD characterization



Amorphous zirconia crystallizes to tetragonal zirconia. GQDs did not affect phases.

Material	Crystal size (nm)	Lattice parameter (A) a	c
ZrO_2	19.4±0.4	3.596	5.185
Ce-ZrO_2	14.6±0.3	3.635	5.227
0.5 wt. % Aminated GQD-Ce-ZrO_2	14.3±0.3	3.636	5.228
0.5 wt. % Carboxylated GQD-Ce-ZrO_2	15.0±0.3	3.635	5.226

Samples were calcined at 700 °C.

Average crystal size of zirconia decreased to ~15 nm from ~19 nm with the addition of ceria. GQDs did not affect the crystal size.

XRD characterization was performed at SJSU using a Rigaku Ultima III X-Ray diffractometer with a Cu Kα radiation source.

XPS characterization

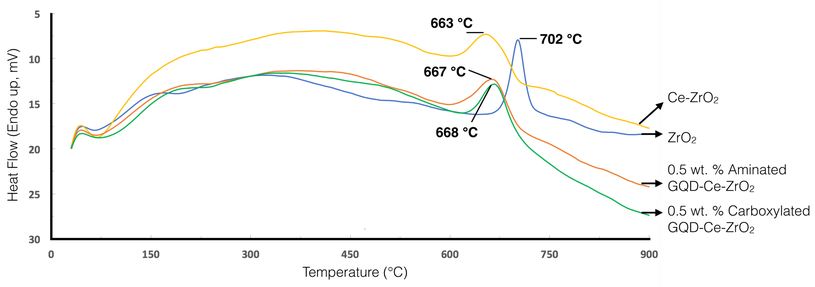
Sample	Ce 3d %	Zr 3d %	O 1s %	C 1s %	Ce/CeZr %
ZrO_2	0.0	17.1	82.0	0.4	0.0
$Ce_{0.16}Zr_{0.84}O_2$	2.4	15.6	81.4	0.6	13.3
$Ce_{0.16}Zr_{0.84}O_2$ 0.1 wt.% Aminated GQD	2.4	15.6	81.9	0.0	13.3
$Ce_{0.16}Zr_{0.84}O_2$ 0.1 wt.% Carboxylated GQD	2.5	15.6	81.6	0.2	13.8
$Ce_{0.16}Zr_{0.84}O_2$ 0.5 wt.% Aminated GQD	2.4	15.6	81.3	0.5	13.3
$Ce_{0.16}Zr_{0.84}O_2$ 0.5 wt.% Carboxylated GQD	2.6	16.3	80.3	0.6	13.8

The reduction reaction targeting 16 at. % Ce-ZrO2 resulted in 13-14 at. % Ce w/ or w/o the GQDs.

XPS characterization was performed at Nanolab Technologies (CA 95035) using a Thermo Scientific K-Alpha XPS system equipped with an Al Kα X-ray source under ultra-high vacuum. A 400 μm spot size was used with a take-off angle of 90°.

DSC characterization

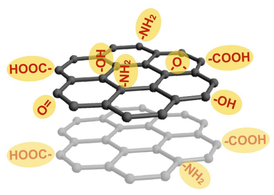
Amorphous-to-tetragonal phase transition temperature was decreased ~40 °C with the addition of ceria. GQDs did not affect the phase transition temperature.

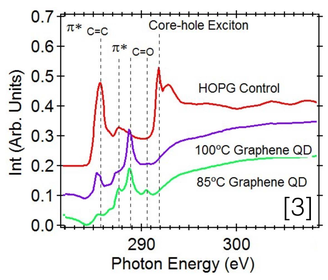


Differential Scanning Calorimetry (DSC) were performed at Perkin Elmer (CA 95134) using a Perkin Elmer Simultaneous Thermal Analyzer STA8000 with N_2 gas flow. The temperature range was 30-900 °C at a heating rate of 10 °C min^{-1}.

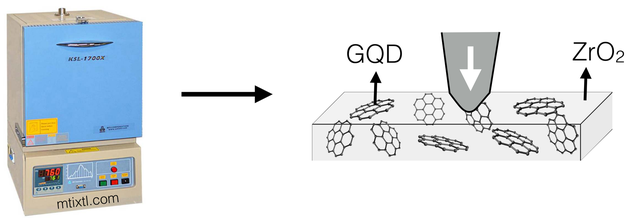
Future work

- Investigate functional groups of GQDs via synchrotron NEXAFS.

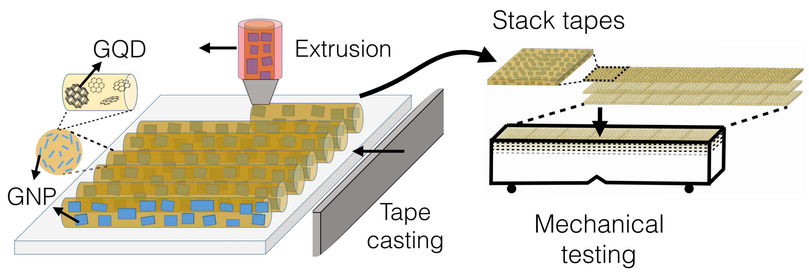




- Investigate effects of GQDs wt. %, functional groups, and size on sintering behavior of Ce-ZrO_2 and indentation toughness.



- Investigate multi-scale toughening mechanisms in GQD-GNP containing systems produced by a combined extrusion-tape casting method.



References

1. Nayak, Nadiya B., and Bibhuti B. Nayak. "Aqueous sodium borohydride induced thermally stable porous zirconium oxide for quick removal of lead ions." *Scientific reports* 6 (2016): 23175.
2. Gobi, N., Vijayakumar, D., Keles, O. and Erogbogbo, F., 2017. Infusion of graphene quantum dots to create stronger, tougher, and brighter polymer composites. *ACS Omega*, *2*(8), pp. 4356-4362.
3. Bokare, A., Wolcott, A., Keles, O., and Erogbogbo, F., Near-Edge X-Ray Absorption Fine Structure (NEXAFS) Investigation of Graphene Quantum dots: Insight into surface functionality, formation mechanisms and synthesis temperature, to be submitted to *Carbon*.