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Processing and Characterization of Ceria-Zirconia Containing Graphene Quantum Dots

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PROCESSING AND CHARACTERIZATION OF CERIA-ZIRCONIA CONTAINING
GRAPHENE QUANTUM DOTS

A Thesis

Presented to

The Faculty of the Department of Chemical and Materials Engineering

San José State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Andrew Dina

December 2020

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The Designated Thesis Committee Approves the Thesis Titled

PROCESSING AND CHARACTERIZATION OF CERIA-ZIRCONIA CONTAINING
GRAPHENE QUANTUM DOTS

by

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APPROVED FOR THE DEPARTMENT OF CHEMICAL
AND MATERIALS ENGINEERING

SAN JOSÉ STATE UNIVERSITY

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ABSTRACT

SODIUM BOROHYDRIDE SYNTHESIS AND CHARACTERIZATION OF CERIA-ZIRCONIA COPRECIPITATE WITH GRAPHENE QUANTUM DOTS

by Andrew Dina

Zirconia-based nanoparticles have been used in various applications, such as catalyst, filters, oxygen storage, and sensors. Among many synthesis methods to produce zirconia (ZrO_2) nanoparticles, aqueous sodium borohydride (NaBH_4) precipitation has shown to be simple and capable of large-scale production. In this work, the NaBH_4 precipitation of ZrO_2 was extended to include ceria (CeO_2) and graphene quantum dots (GQDs). The resulting nanocomposites were characterized by thermal, crystallographic, compositional, and electron microscopy analysis techniques. The presence of CeO_2 lowered the amorphous to tetragonal phase transformation temperature by $\sim 40^\circ\text{C}$. The presence of GQDs did not affect the amorphous to tetragonal transformation temperature. In addition, cerium ions were inserted into the ZrO_2 lattice with an increase to the interplanar spacing, seen by a slight shift in the diffraction peaks with no new peaks. Compositional analysis showed a stoichiometry between 13-14 mol. % ceria in the ZrO_2 matrix with no elevated carbon concentration consistent with GQD doping levels. Agglomerated particles of several crystallites were observed and the presence of CeO_2 increased the degree of agglomeration. The presence of GQDs was not conclusive, diffraction measurements were close to the theoretical value for the GQD basal plane, however, observation of the nanoparticles were not clear. More studies are needed to conclude the presence and functional interaction of GQDs and their role in nano-particle synthesis-structure relationships.

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LIST OF ABBREVIATIONS

2-CEES – 2-chloroethyle ethyl sulfide
BET – Brunauer-Emmett-Teller
BJH – Barrett-Joyner-Halenda
 $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ – cerium chloride heptahydrate
 CeO_2 – ceria
 Ce-ZrO_2 – ceria-zirconia
CTAB – cetyltrimethylammonium bromide
DI – deionized
DSC – Differential Scanning Calorimetry
EDS – Energy Dispersive Spectroscopy
Eu – europium
GQDs – graphene quantum dots
GQD-Ce-ZrO₂ – ceria-stabilized zirconia containing GQDs
HRSEM – High Resolution SEM
HRTEM – High Resolution Transmission Electron Microscope
IPA – isopropyl alcohol
 La_2O_3 – lanthana
 NaBH_4 – sodium borohydride
 m-ZrO_2 – monoclinic zirconia
 OH^- – hydroxyl
OSC – oxygen storage capacity
PPE – personal protective equipment
PSZ – partially stabilized zirconia
Pt – platinum
SDS – safety data sheets
SEM – Scanning Electron Microscopy
Sr – strontium
TEM – Transmission Electron Microscopy
TGA – Thermogravimetric Analysis
 TiO_2 – titania
TPR – Temperature Program Reduction
TZP – tetragonal zirconia polycrystals
 t-ZrO_2 – tetragonal zirconia
XPS – X-ray Photoelectron Spectroscopy
XRD – X-ray Diffractometry
 ZrO_2 – zirconia
 Zr(OH)_4 – zirconium hydroxide
 $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ – zirconium oxychloride octahydrate

CHAPTER ONE

INTRODUCTION

Zirconium dioxide (ZrO_2)-based ceramics have been a popular material of choice for a variety of industries due to outstanding material characteristics. High mechanical strength, toughness, wear and corrosion resistance make ZrO_2 -based ceramics optimal in structural and bearing applications [1]. Due to its high thermal resistance to shock and low thermal conductivity, zirconias are a good choice for the refractory and coatings industries [1]. In addition, ZrO_2 -based ceramics have become the dominant ceramic of choice in the biomedical industry for applications like medical and dental implants due to superior biocompatibility and mechanical properties [2]. Also, in the presence of oxygen, ZrO_2 -based ceramics have been very stable making them a good choice in oxygen rich systems such as fuel cells and oxygen sensors for the fuel and automotive industries [3]. In addition, zirconia has been used in optical applications such as photonics, interferometry filters, and laser mirror coatings due to its hardness, optical transparency and refractive index [4]. ZrO_2 -based ceramic systems usefulness across a large number of applications can be attributed to the dominant material properties within its different phases and unique properties.

1.1 Zirconia

ZrO_2 is a white crystalline oxide that naturally occurs in the form of mineral baddeleyite [5]. As a polymorph, it holds three crystalline phases; monoclinic stable below 1170 °C, tetragonal stable between 1170-2370 °C, and cubic stable above 2370 °C [2]. Each phase holds different dominant material properties best tailored for a variety of

applications. In order to utilize high temperature phases at lower temperature applications, these phases must be in a stabilized state, or metastable state [6]. There have been a variety of mechanisms proposed to explain these metastable states: either thermodynamic factors influenced by particle size, surface area, and surface tension [7,8], or kinetic factors such as impurities, vacancies, and lattice defects [9–12]. For example, tetragonal zirconia ($t\text{-ZrO}_2$) particles below a critical size of ~ 30 nm stabilize at room temperature, above which the surface free energy drives transformation to the monoclinic zirconia ($m\text{-ZrO}_2$) phase [7].

How we synthesize ZrO_2 plays an important role in stabilizing a phase and has been extensively investigated [1,4,13–15]. Different synthesis techniques, such as sol-gel, spray pyrolysis, calcination, and precipitation, have been reported to affect crystal phases and morphology [4,8,16,17]. For example, a metathesis reaction yields either rod-like tetragonal or spherical shaped cubic ZrO_2 particles by merely changing the method of mixing the precursors prior to thermal treatment [17]. Among these synthesis techniques, precipitation methods are simple and suitable for large scale production [1,18]. One of these precipitation synthesis techniques uses sodium borohydride (NaBH_4) to reduce zirconium oxychloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) to zirconium hydroxide ($\text{Zr}(\text{OH})_4$) [18–20]. This reduction reaction produces amorphous ZrO_2 with heat-treatment below 400°C [18–20]. The NaBH_4 synthesis occurs at room temperature [19]; hence, offers flexibility of using surfactants, dopants, and second phases to tailor final ZrO_2 structure and composition for particular applications [18–20].

1.2 Partially Stabilized Zirconia

Another method for controlling phase stabilization of ZrO_2 has been the use of surfactants and dopants. For example, the addition of cetyltrimethylammonium bromide (CTAB) surfactant produced flake-like t- ZrO_2 particles [18]. There is a two-pronged challenge with using surfactants. First, the surfactant can have unintended reactions during either synthesis or application. Second, surfactants are not the best method for addressing the large volume change inherent with ZrO_2 phase changes. In both manufacturing and applications, ZrO_2 's high fracture toughness and hardness is due to transformation toughening, a reversible martensitic tetragonal-to-monoclinic phase change when subjected to either stress or heat [21]. There is a 4-5 % volume change during this transformation that can cause inter-granular fracture [21]. However, dopants have been found to both stabilize high temperature phases at lower temperatures while allowing the material to withstand the large volume change during phase transformation [9,21].

Coined partially stabilized zirconia (PSZ), dopants like calcia, yttria, magnesia, and rare earth metals have shown to stabilize ZrO_2 while improving a variety of material properties [22–24]. Among one of the first, small amounts of yttria doping has been used to stabilize tetragonal zirconia polycrystals (TZP) while increasing mechanical properties like strength, hardness, and toughness [25]. Ceria (CeO_2) has been one of the most promising and fruitful stabilizing dopants for its ability to enhance ZrO_2 unique transformation toughening effect [25]. It was reported the fracture toughness almost doubled from 4 to 7 $\text{MPa}\cdot\text{m}^{1/2}$ due to transformation behavior when TZP was stabilized

with 18 mol% CeO₂ [26]. Since then, CeO₂-stabilized zirconia (Ce-ZrO₂) based systems have received a large amount of research to expand and optimize material properties for a variety of applications [27–31].

1.3 Second Phase Dopants

Secondary phase dopants can also tailor material properties for particular applications of ZrO₂-based nanocomposites. Specifically, carbon-based second phases have been reported to affect various properties like optical, electrical, catalytic, and mechanical [32–35]. For example, the photocatalytic efficiency of ZrO₂ was almost doubled when doped with 8.3 wt. % graphene [32]. Additionally, doping yttria-ZrO₂ with greater than 2.2 vol. % of graphene nanoplatelets decreased the composite hardness, suppressed the formation of tetragonal phase, and increased the electrical conductivity [33].

Unlike larger carbon-based secondary phases, graphene quantum dots (GQDs) are a relatively new material that are smaller than 10 nm in diameter with a single to a few layers of graphene [36,37]. GQDs are used for bioimaging, biomarking, drug delivery, fluorescent sensing, and photovoltaics due to their biocompatibility, photoluminescence, and electronic properties [38–44]. By changing the size, shape, and functional groups of GQDs, photoluminescence behavior has been adjusted to cover the ultraviolet to near infrared emission spectrum range [38,39].

The use of GQDs as a secondary phase dopant has the potential of optimizing particular material properties tailored for engineering applications. For example, GQDs were reported to increase toughness, elastic modulus, and tensile strength of epoxy with the addition of 1.0 to 2.5 wt. % of GQDs [45]. GQDs were also reported to increase the

electrical conductivity and hardness of cellulose acetate films [46]. With respect to metal-oxide ceramics, an increase in visible light absorption and photocatalytic activity in anatase titania (TiO_2) with GQDs was reported [47]. If GQDs were added to PSZ, there could potentially be an increase in toughness that perhaps would reduce the intergranular fracture inherent during transformation toughening. This speculative result could in turn mean higher degree of shape memory deformation with larger elongation before fracture. The processability of PSZ ceramics containing GQDs are unclear in the literature and warrant investigation.

In this work, previously synthesized Ce- ZrO_2 nanoparticles doped with GQDs were characterized. NaBH_4 precipitation derived ZrO_2 , Ce- ZrO_2 and Ce-stabilized ZrO_2 containing GQDs (GQD-Ce- ZrO_2) were analyzed. In addition, two different GQDs with amine and carboxyl functional groups were used to observe the effects functional groups had on morphology and structure of ZrO_2 . Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to observe the phase behavior, while X-ray diffractometry (XRD) was used to identify the associated crystalline phases. X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM), coupled with energy dispersion spectroscopy (EDS) were used to characterize the composition, size, structure, and bonding states of the nanoparticles. And lastly, scanning electron microscopy (SEM) was used to observe the morphology of the resulting ZrO_2 -based ceramic composites.

CHAPTER TWO

LITERATURE REVIEW

2.1 Zirconia Nanomaterials

Since the first reporting of metastable t-ZrO₂ in 1929 [48], much research has been done to understand how metastable phases are obtained. Garvie was among the first to use experimental work and thermodynamics to explain the relationship between crystallite size and low temperature metastable t-ZrO₂ phase [7]. With two synthesis methods, precipitation of zirconyl nitrate and sodium hydroxide to produce a hydrous oxide [7], and calcination by thermal treatment of the anhydrous nitrate at 400 °C for 48 hours, Garvie produced metastable t-ZrO₂ [7]. To study the phase dependency, both samples were heated in air at various temperatures up to 1000 °C for 24 hours [7]. XRD analysis showed a transition from tetragonal to monoclinic as thermal treatment increased, as shown in Figure 1a [7]. Precipitation held the tetragonal phase at higher annealing temperatures than calcination, showing signs of monoclinic transformation at approximately 700 °C, and complete monoclinic phase at approximately 775 °C [7]. The calcined oxide started developing monoclinic phase at approximately 525 °C and complete monoclinic phase at approximately 800 °C [7]. Figure 1b is a graphical representation of the average t-ZrO₂ crystallite size with respect to temperature [7]. As the heating temperature increased, the average crystallite size for both samples converged near 30 nm, above which both samples transformed completely to monoclinic phase [7]. Brunauer-Emmett-Teller (BET) was used to obtain the specific surface area for each sample at various heating temperatures in order to thermodynamically correlate crystallite

size and phases [7]. As the crystallite size increased, the specific surface area and excess energy decreased, both near a minimum of about 30 nm, Figures 2a and 2b, respectively [7]. These results suggested there was an equilibrium between the tetragonal and monoclinic phases at a crystallite size of about 30 nm [7]. Equation 1 is the relationship in terms of molar free energy (G), surface energy (γ), and molar surface (A), where subscripts t and m denote tetragonal and monoclinic, respectively [7]. This study suggests two different synthesis methods can stabilize t-ZrO₂ at room temperature when the average crystallite size is less than 30 nm with appreciable surface area and excess energy [7].

$$G_m + \gamma_m A_m = G_t + \gamma_t A_t \quad \text{Equation 1}$$

Figure 1. XRD phase (a) and crystallite size (b) results with increasing calcine temperature [7].

Figure 2. Specific surface (a) and excess energy (b) as a function of crystallite size for precipitated and calcined samples compared to theoretical values [7].

The transformation behavior of metastable ZrO_2 is influenced by what synthesis method is used. In another study, Djurado *et. al.* used a spray-pyrolysis method with different post synthesis calcination temperatures to show a relationship between crystallite size and metastable tetragonal-monoclinic phase transformations [8]. An ultrasonic atomizer with a mist generator operating at 850 kHz and 1.7 MHz frequencies was used to produce two samples with starting average crystallite sizes of 6.9 and 13.2 nm, respectively [8]. Table 1 is a tabulation of the synthesis conditions used to produce the two batches [8]. The samples were then annealed in platinum (Pt) crucibles for temperatures ranging from 600-1400 °C at a heating rate of 5 °C min⁻¹ for times ranging from 15 minutes to 2 hours [8]. Table 2 shows the annealing temperatures and times for the two sample types with their resulting crystallite sizes [8]. Utilizing XRD and Raman spectroscopy, it was found that the critical size effect for a particular phase varied with preparation, moisture concentration, and percent of phases present prior to annealing [8]. The 6.9 nm starting sample had approximately 5 % monoclinic phase whereas the 13.2 nm starting sample was less than 1 %, if any due to the resolution of the technique [8]. The presence of monoclinic phase prior to annealing yielded a faster transformation to monoclinic phase at lower temperatures, even at smaller crystallite sizes [8]. Figure 3 is the XRD results for the various samples in this study and shows this synthesis method produces nanoparticles of both tetragonal and monoclinic phases with only a difference in the synthesis parameters [8]. In addition, either the smaller crystallite size or the presence of monoclinic phase caused a gradual transformation with increasing annealing temperatures, whereas the larger starting crystallite size showed a sudden tetragonal to

monoclinic phase transformation [8]. Unfortunately, a surface area study was not conducted, as it may have offered an interesting explanation to the varying phase transformation behaviors between the different starting crystallite size samples, or at the least showed support for or against Garvie's thermodynamic explanation.

Table 1. Spray pyrolysis conditions and resulting crystallite size measured from x-ray line broadening for two batches of ZrO₂ powders [8].

Batch No.	Concentration (mol L ⁻¹)	Frequency (kHz)	Flow rate (L min ⁻¹)	Temperature (°C)	Crystallite size (nm)
I	2.5 x 10 ⁻²	1.7 x 10 ³	6	600	6.9
II	2.5 x 10 ⁻²	850	3	900	13.2

Table 2. Referred samples for two batches of ZrO₂ powders [8].

Annealing conditions in air	Batch I, Crystallite size (nm)	Batch II, Crystallite size (nm)
No annealing	6.9	13.2
600 °C, 15 min	8.3	13.8
600 °C, 2 h	8.9	13.3
800 °C, 2 h	20.3	18.0
900 °C, 15 min	21.0	21.8
950 °C, 1 h	30.1	22.0
1000 °C, 1 h	36.3	25.5
1400 °C, 2 h	65.2	85.8

Figure 3. X-ray diffractograms of (a) I-6.9 and (b) II-13.2 versus crystallite size increase [8].

Like Djurado's research showed, the starting phase composition makes a difference even at sub room temperature conditions. Bouvier *et. al.* continued the study of Djurado by investigating sub room temperature phase stability and any correlation with crystallite size for ZrO_2 samples produced by the same spray pyrolysis synthesis method [13]. Three samples with different average crystallite sizes, 6.9, 13, and 18 nm, were analyzed using Raman and neutron scatter spectroscopy techniques through a temperature range of 296 K to 96 K [13]. Figure 4 is the Raman spectra for the 6.9 and 18 nm samples [13]. The broadness of the peaks for the 6.9 nm sample indicated the presence of an initial 5 % monoclinic phase and the broadening of the shoulder around 350 cm^{-1} indicated an increased monoclinic concentration with decreasing temperature [13]. It was also noted

that upon returning to room temperature, 6.9 nm sample returned back to its initial state suggesting a reversible structural evolution with a crystallite size at least as small as 6.9 nm [13]. The 13 and 18 nm sample spectra were virtually identical and showed no significant change through the temperature range indicating t-ZrO₂ is stable at low temperatures with a crystallite size as low as 13 nm [13].

Figure 4. Raman spectra for 6.9 nm (a) and 18nm (b) ZrO₂ versus temperature [13].

In another study, Kumar and coworkers researched a sol-gel synthesis method to produce ZrO₂ nanostructures at different calcination temperatures that also resulted with a mixture of phases [4]. By varying the calcination temperature, they were able to show that not only can different phases be achieved but different morphologies as well [4]. ZrOCl₂·8H₂O was dissolved in distilled water and an ammonia solution was added dropwise to precipitate a Zr(OH)₄ solution [4]. Calcination of the solution for three hours finalized the synthesis process of ZrO₂ nanoparticles [4]. Calcination at 500 °C yielded pure tetragonal phase with a crystallite size of about 8 nm and a spherical morphology

[4]. Calcination at 600 °C yielded a mixture of 73 % tetragonal and 27 % monoclinic phases with an average crystallite size of 17 nm and a spherical morphology [4]. The sample calcined at 700 °C also had a combination of 36 % tetragonal and 64 % monoclinic phases but had a reduced crystallite size of 10 nm with a rod like morphology [4]. Figure 5 shows TEM micrographs and histograms of the morphology and size of the three samples [4].

Figure 5. TEM micrographs and histograms of ZrO₂ nanostructures calcined at 500, 600, and 700 °C [4].

Contrary to the crystallite size effect observed in the research above, Grover et. al. showed that stabilized t-ZrO₂ particles can be achieved with different morphologies and crystallite sizes in the micron range [17]. Grover and coworkers used two synthesis methods to produce ZrO₂ particles with different morphologies [17]. The first method was simply to sprinkle zirconium oxychloride (ZrOCl₂) powder over sodium hydroxide (NaOH) pellets and heat the mixture at 400 °C for 4 hours [17]. The resulting material

was noted to self-separate into sodium chloride and ZrO_2 where XRD and SEM analysis showed a t- ZrO_2 phase with rod-like shaped particles having diameters of about 100 microns [17]. The second synthesis method ground the two precursors together, rinsed and dried them at 120 °C resulting in spherical shaped t- ZrO_2 particles of sizes ranging between 1-5 microns [17]. Figure 6 is SEM micrographs of the resulting morphologies of the two different synthesis methods of t- ZrO_2 [17].

Figure 6. SEM micrographs of the first synthesis method with rod-like particles (left), and the second synthesis method showing spherical shaped particles (right) [17].

Of all the synthesis methods, precipitation has been shown to simplify the process along with reduce the time and energy needed for production of ZrO_2 nanoparticles [1]. Guo *et. al.* developed a precipitation process to produce zirconium oxy-hydroxy-acetate from readily available zirconium oxychloride and acetic acid [1]. By simply mixing the two with constant stirring and pH monitoring, zirconium oxy-hydroxy-acetate was produced [1]. After aging for two days, washing with DI water and drying at 70 °C for 56 hours, the solution was ready to anneal at various temperatures to observe the ability to form ZrO_2 nanoparticles [1]. DSC, TGA, and XRD were used to identify the thermal

events that occurred over the temperature range of room temperature to 800 °C [1].

Figures 7 and 8 are the DSC/TGA and XRD results, respectively [1]. XRD analysis for the as prepared sample was found to be amorphous with absence of any diffraction peaks [1]. TGA weight loss observed from room temperature up to about 396 °C was primarily attributed to dehydration of the sample where the first thermal event at 119 °C was from desorption of physically absorbed water [1]. The second thermal event at 396 °C was attributed to decomposition of the acetate complex and XRD results show formation of some t-ZrO₂ with an average crystallite size of 24.3 nm [1]. Further heating to 545 and 710 °C revealed increased tetragonal crystallinity with an increasing presence of the monoclinic crystalline phase and increased crystallite sizes of 30.4 and 113.1 nm, respectively [1]. This precipitation process suggests a simple synthesis method that can produce ZrO₂ nanoparticles but does not exhibit pure phase crystallinity.

Figure 7. DSC (solid line) and TGA (dashed line) curves of the zirconium acetate-complex [1].

Figure 8. XRD patterns of the zirconium acetate-complex for, (a) as synthesized, calcined at (b) 396, (c) 545, and (d) 710 °C [1].

In 2010, Nayak *et. al.* published a precipitation synthesis process that utilized NaBH_4 as the precipitation agent and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ as the zirconium precursor to produce low temperature t- ZrO_2 with a flake-like morphology [18]. They also included a surfactant, CTAB, to investigate the effects it may have on phase stabilization [18]. This synthesis process was again simplified by adding the $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ solution drop-wise to the NaBH_4 solution during vigorous stirring until a pH of 10 was achieved, the CTAB was added to the $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ solution before adding to the NaBH_4 [18]. The resulting solutions were thoroughly washed with distilled water numerous times until the pH was that of the distilled water, dried at 80 °C in an oven, and then ground to a powder with a mortar and pestle [18]. Figure 9 is the DSC results showing similar dehydration characteristics but with very different crystallization peaks past about 500 °C [18]. Clear and sharp transition peaks were observed in the sample without CTAB, whereas the

transition peaks were not only broadened but also shifted to higher temperatures for the sample with CTAB [18]. Annealing temperatures of 400, 600, 700, and 800 °C were chosen and XRD analysis was conducted to identify the resulting crystallinity [18]. The as-prepared and 400 °C annealed samples were found to be amorphous for samples with and without CTAB [18]. The samples with and without CTAB annealed at 600 °C were found to have some t-ZrO₂ crystallites of about 5 nm in size [18]. Figure 10 is the XRD results for the 700 °C samples with and without CTAB [18]. Pure tetragonal phase with an average crystallite size of 15 nm was found in the CTAB sample. Whereas, majority tetragonal with a small amount (about 5 vol.%) of monoclinic phase with an average crystallite size of 20 nm was found in the sample without CTAB [18]. Further increase of the annealing temperature showed an increase in crystallite size and further progression to monoclinic crystalline phase for both samples [18]. These results suggest CTAB can better stabilize t-ZrO₂ nanoparticles rather than without CTAB, however, it increases the phase transformation temperature to achieve the tetragonal phase.

Figure 9. DSC curves for as-synthesized ZrO_2 powders (a) with and (b) without CTAB [18].

Figure 10. XRD results of ZrO_2 powders with and without CTAB annealed at 700 $^{\circ}\text{C}$ [18].

Nayak *et. al.* realized the NaBH_4 precipitating agent had an advantage over many other precipitating agents used to produce ZrO_2 nanoparticles, which could be applied in industrial and commercial uses [20]. In addition to phase separation to form boron free ZrO_2 , they observed the borohydride complex evolved hydrogen gas bubbles during precipitation, which resulted in porous ZrO_2 nanoparticles that could be used for absorption and storage applications [20]. This study focused on understanding the in-situ hydrogen gas bubble evolution and the resulting absorption performance of t- ZrO_2 for lead (Pb II) ion removal in a water solution [20]. A wide pore size distribution between 3.6 to 15.8 nm was reported with an average pore diameter of 4.6 nm [20]. Lead ion removal efficiency was reported to be about 99% in only 15 minutes [20]. Chromium (Cr VI) ions were also used to determine if there is a diversity to toxic metal ion removal and a reported efficiency of about 10% suggesting porous ZrO_2 was not diverse [20].

2.2 Ceria-Zirconia Nanomaterials

In addition to synthesis techniques for production of metastable ZrO_2 phases, stabilizers like yttria, magnesia, calcia, and CeO_2 can be used with an added bonus of tailoring material properties [5]. Borik *et. al.* illustrated t- ZrO_2 could be produced by directional melt crystallization growth with 2.8-5.0 mol. % yttria doping [5]. The resulting PSZ had increased fracture toughness and hardness due to the martensitic transformation toughening to monoclinic phase under increased stress [5].

Quan *et.al.* looked into the effects europium (Eu) doping would have on ZrO_2 [24]. SEM analysis revealed spherical nanoscale particles were made by using a spray pyrolysis and post annealing synthesis technique [24]. XRD analysis showed the onset of

crystallinity with an annealing temperature as low as 400 °C and a metastable t-ZrO₂ phase with Eu³⁺ ions placed in substitutional lattice sites [24]. Photoluminescent intensity was found to increase with increasing annealing temperature with a maximum performance of 10 atomic % Eu doping [24]. The use of dopants can play a double roll, stabilizing high temperature ZrO₂ phases at low temperatures, and tuning material properties for particular applications.

CeO₂ has been a popular stabilizing agent for t-ZrO₂ due to high solubility and phase stabilization even at larger grain sizes [25]. Tsukuma and colleague studied the mechanical behavior of TZP containing 7-16 mol % CeO₂ at different grain sizes [25]. They produced hydrous CeO₂- ZrO₂ powders by a hydrolysis method of mixing cerium chloride with zirconyl chloride and heating at 100 °C for 50 hours [25]. Thermal treatment up to 950 °C was still able to retain the tetragonal phase which served well for sintering samples for mechanical testing [25]. They found there was an optimal CeO₂ concentration for different mechanical properties [25]. The bending strength saw a maximum around 800 MPa when doped with 12 mol % CeO₂ with a 1.0 µm average grain size [25]. The fracture toughness was somewhat opposite with a maximum K_{IC} of about 17.5 MNm^{-1.5} at 8 mol % CeO₂ concentration and 2.5 µm average grain size [25]. Lastly, Vickers hardness was found to decrease with increasing average grain size and decreasing CeO₂ concentration [25]. The presence of CeO₂ not only stabilized the tetragonal phase of ZrO₂ at room temperature, but even stabilized when cooled after sintering with resulting large grain growth [25]. Unfortunately, this study did not report

crystallite size to compare with the observed 30 nm critical crystallite size for stabilization of t-ZrO₂.

Cerium has played a large roll in modern catalysts due to its oxygen absorption and desorption capability and researchers have investigated the effects of incorporating CeO₂ with ZrO₂. Chen and colleagues investigated the porous nature of Ce-ZrO₂ materials for possible catalytic applications [49]. BET analysis showed ZrO₂ alone had a specific surface area of 362 m²s⁻¹ whereas ZrO₂ containing CeO₂ had 268 m²s⁻¹ [49]. H₂ absorption analysis gave comparable pore volumes of 0.163 and 0.132 cm³g⁻¹ for the pure ZrO₂ and Ce-ZrO₂ samples, respectively [49]. And XRD results showed CeO₂ was placed into the substitutional sites of the ZrO₂ lattice with a slight reduction in lattice interplanar spacing from 3.14 to 2.97 nm [49]. It was concluded that the addition of CeO₂ into the ZrO₂ lattice would reduce the specific surface area while maintaining pore volume suggesting an impact in the pore hysteresis [49].

Aribi *et. al.* further researched the effects doping ZrO₂ with CeO₂ would have on structure and catalytic properties [50]. Using a hydrolysis synthesis method, they found increasing the CeO₂ concentration and annealing temperature decreased the specific surface area [50]. At the same time, the addition of CeO₂ decreased the pore size compared to pure CeO₂ or ZrO₂ alone [50]. Furthermore, increasing the CeO₂ concentration increased the H₂ uptake in H₂-Temperature Program Reduction (TPR) analysis while increasing annealing temperatures did not show a significant difference [50]. The addition of CeO₂ played a majority roll in increasing the absorption of ZrO₂ nanoparticles even though the pore size reduced with increasing CeO₂ concentration [50].

Guillén-Hurtado and coworkers also investigated a Ce-ZrO₂ mixed oxide system to compare two different cerium based precursors for incorporation of Ce³⁺ and Ce⁴⁺ ionic species [51]. Ce-ZrO₂ mixed oxides with three different molar ratios (Ce_{0.8}Zr_{0.2}O₂, Ce_{0.5}Zr_{0.5}O₂, Ce_{0.2}Zr_{0.8}O₂) along with pure ZrO₂ and pure CeO₂ were analyzed for this study [51]. The samples with ZrO₂ content up to 50 mol% using the Ce⁴⁺ precursor were found to coprecipitate well, whereas the samples using the Ce³⁺ precursor had poor insertion of ZrO₂ into the lattice system [51]. Calcination at 1000 °C lead to segregation of tetragonal and cubic phases for the samples using the Ce³⁺ precursor and a single cubic phase for the samples using the Ce⁴⁺ precursor [51]. Greater oxygen mobility was observed in the samples synthesized with the Ce⁴⁺ precursor due to a higher number of defects and atomic homogeneity [51].

In another study, Chen *et. al.* noted that Ce-ZrO₂ material systems could be used as a reactive sorbent for degrading chemical species [27]. Their study focused on synthesis of the Ce-ZrO₂ materials and the degradation of 2-chloroethyle ethyl sulfide (2-CEES), a simulating agent for mustard gas [27]. Table 3 lists the samples that were prepared using a precipitation method with ammonia as the precipitating agent and calcined at 400 °C for 6 hours [27]. XRD results showed CeO₂ cubic-fluorite structure with increasing shift in the 2-theta peaks with increasing ZrO₂ concentration indicating ZrO₂ assuming substitutional lattice sites [27]. BET and Barrett-Joyner-Halenda (BJH) utilizing nitrogen absorption/desorption isotherm were used to characterize the mesoporous nature of the synthesized samples and the results are listed in Table 3, where the particles were noted to have type IV adsorption isotherms with H3 type porous hysteresis loops [27]. Figure

11 illustrates the degradation kinetics of 2-CEES where the Ce:Zr atomic ratio of 1:1 degraded 82% in 4 hours, outperforming all other samples [27]. Even with a different phase structure, the combination of CeO₂ and ZrO₂ can serve to improve performance for particular applications.

Table 3. Structure and degradation properties for Ce-ZrO₂ co-precipitation material systems [27].

Sample	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Mean pore size (nm)	Rate constant k_1 (h ⁻¹)	Half-life of 2-CEES $t_{1/2}$ (h)
CeO ₂	142	0.52	14.3	6.56×10^{-1}	1.06
Ce _{0.67} Zr _{0.33} O ₂	156	0.34	8.1	6.98×10^{-1}	0.99
Ce _{0.5} Zr _{0.5} O ₂	155	0.43	10.6	4.84×10^{-1}	1.43
Ce _{0.33} Zr _{0.67} O ₂	140	0.29	7.7	6.99×10^{-1}	0.99
ZrO ₂	73	1.04	55.8	1.97×10^{-1}	3.52

Figure 11. Degradation kinetics of 2-CEES for Ce-ZrO₂ co-precipitation material systems [27].

2.3 Doped Ceria-Zirconia Nanomaterials

With evidence Ce-ZrO₂ systems had increased material performance, interest turned to further addition of other dopants for even greater material property refinement. Environmentally friendly hydrogen has been proposed as a sustainable fuel that can possibly replace fossil fuels and thus has received large interest in the scientific communities [52]. Ce-ZrO₂ nanomaterials have been found to be a good foundation for hydrogen production by a water splitting reaction [52]. Dasari *et. al.* researched the enhancement of hydrogen production when a Ce-ZrO₂ system was further doped with rare-earth (RE) metals [52]. Increased hydrogen production was observed when Ce-ZrO₂ composites were doped with either terbium, praseodymium, or lanthanum, with the highest production enhancement from praseodymium at 205 $\mu\text{mol/g}$ [52]. The enhanced performance of praseodymium was further confirmed with the highest oxygen storage capability of 155 $\mu\text{mol/g}$ [52]. Because the systems contained majority CeO₂ (65 mol%), XRD results confirmed a cubic-fluorite crystalline structure with the same shifting 2-theta peak trend that correlated to the difference in ionic radii of the dopant elements as reported in previous work [27,52]. Confirmation the RE dopants were substitutional placed into the Ce-ZrO₂ lattice was obtained by no presence of new peaks in the XRD results [52]. Raman spectroscopy results showed praseodymium had a higher intensity than the other RE dopants signifying an improvement in oxygen mobility and in turn catalytic activity which correlated with the oxygen storage and hydrogen production results [52].

Oxygen storage capability of Ce-ZrO₂ composites have become a point of focus for researchers due to higher performance in purification of immersion gases like carbon monoxide and hydrocarbons [31]. Fan *et. al.* studied the oxygen storage capability of Ce-ZrO₂ systems with a 2:1 ratio when modified by either coprecipitation or impregnation of 3 mass percent strontium (Sr) and when thermally aged or not [31]. All samples were annealed at 700 °C and XRD analysis indicated a cubic-fluorite crystalline phase [31]. The thermally aged samples were further annealed at 1050 °C for 5 hours and the sharpening of the XRD peaks indicated sintering of the powders [31]. In addition, the presence of new peaks indicated segregation of CeO₂ and ZrO₂ rich phases [31]. The sintering and segregation effects from thermal aging were reduced by the addition of Sr by either introduction method but the impregnation method showed greater thermal stability [31]. The correlation between reducibility and activation energy were observed in this study when the aged Sr impregnated Ce-ZrO₂ samples had the greatest reducibility and greatest oxygen storage capacity (OSC) [31]. Because segregation was observed in this sample, it was suspected that the interface between SrZrO₂ and CeO₂-ZrO₂ offered the greatest oxygen mobility and held highly active oxygen species resulting in maximum performance [31]. Having a secondary alloying phase, such as the impregnated Sr in this case, could serve to help tailor the overall material performance for particular applications. The implementation of further system doping and secondary phase doping has the possibility of enhancing Ce-ZrO₂ performance and tailoring the systems properties for particular applications.

2.4 Carbon, Graphene and Quantum Dots

Due to being environmentally friendly and because it is abundantly available, carbon-based materials have received great interest in research communities. Research into carbon-ZrO₂ nanocomposites and other material systems were used to gain some insight for developing this project due to the infancy of GQDs and limited published research. Kaur et. al. investigated the hydrogen storage capability of ZrO₂ and reduced graphene oxide nanocomposites for applications in fuel cell and similar technologies [35]. Enhanced hydrogen storage capacity for ZrO₂-reduced graphene oxide versus graphene oxide was found to be due to the changes in surface area and porosity [35]. They observed an increase in surface area from 14.3 m²/g for graphene oxide to 390 m²/g for ZrO₂-reduced graphene oxide [35]. Additionally, they observed a decrease in pore size distribution from 5.38 nm for graphene oxide to 2.56 nm for ZrO₂-reduced graphene oxide [35]. Some insight this research offered was the increase in thermal stability and presence of oxygen functional groups with the ZrO₂-graphene oxide composite system [35], suggesting reasonable investigation into thermal stability and preservation of functional groups for ZrO₂-GQD composite systems.

The work done by Rani et. al. offered further supporting evidence for thermal stability and preservation of functional groups for ZrO₂-graphene composite systems [32]. Zirconia oxychloride precursor in a precipitation and reflux synthesis method with post annealing treatments up to 1000 °C was used to produce the ZrO₂-graphene composite [32]. Their work showed the addition of graphene to ZrO₂ increased the photocatalytic activity of ZrO₂ for the degradation of methyl orange with increasing

content of graphene in the composite system [32]. It was stated that the enhancement in the photocatalytic activity was due to graphene creating electron hole pairs without the ability of recombination, offering more available sites for the photo catalytic reaction to take place [32]. They also reported photocatalytic reactions increased when the annealing temperature increased [32], offering some reasonable suggestion that GQDs could be thermally stable in a ZrO_2 based support and remain after synthesis and thermal treatments.

GQDs are a relatively new founded material and has been projected to have a profound impact for industrial applications due its unique properties [36]. In 2014, Bacon et. al. published an overview covering up-to-date research for synthesis, properties, and applications of GQDs [36]. At that time, GQDs were synthesized by two generally categorized methods, either top-down or bottom-up methods [36]. The top-down method generally starts with converting a graphite based material to graphite oxide sheets by some form of the Hummers method with a mixture of sulfuric acid, sodium nitrate, and potassium permanganate, or similar chemistry [36]. At this point, several different methods could be utilized for converting the graphene oxide sheets to GQDs such as: hydrothermal cutting, solvochemical cutting, electrochemical cutting, nanolithography, microwave-assisted cutting, nanotomy-assisted exfoliation, and ultrasonic shearing [36]. Generally speaking, the alternative bottom-up approach involves pyrolysis of an acid, like citric acid, to produce graphite followed by carbonization, or oxidation exfoliation, to yield GQDs [36]. Bacon covered a stepwise organic synthesis technique where oxidation of polyphenylene dendritic precursors produced large colloidal GQDs [36]. Another

bottom-up approach given was cage opening of fullerenes where catalyzed ruthenium gave attachment sites for C60 to embed on the surface and post annealing treatments agglomerated the carbon clusters to produce GQDs [36].

GQDs hold extraordinary properties, most notable is quantum confinement that results in a non-zero bandgap and luminesce upon excitation [36]. By modification of GQDs with different functional groups and densities, the photoluminescence spectrum can be tailored in the range of ultraviolet to near-infrared [36]. It was noted that one of the most attractive aspects of GQDs was they are a carbon material that are abundantly available, have low toxicity, highly soluble, and can be easily modified by functional groups, making them viable alternative substitutes over their inorganic counterparts for applications [36].

Electrooxidation of graphene to produce GQDs has been promised as an environmentally friendly approach that avoids the use of high temperatures and chemically hazardous reagents [42]. Luo et. al. published new findings for GQDs synthesized using this electrooxidation method, producing GQDs with average diameters of about 52 nm that have photoluminescence excitation wavelength-independent properties [42]. This contradicted earlier findings and motivated Luo to investigate further [42]. By synthesizing more GQDs and using a dialysis bag to separate particle sizes, it was found that this synthesis method also produced smaller sizes of several nanometers that were found to be wavelength-dependent, showing a size dependence on the photoluminescence capability [42].

The implementation of GQDs into polymeric material systems have shown to enhance some material properties while suppressing others, suggesting the ability to tailor composites for particular applications [46]. Using a polymer composite of cellulose acetate and GQDs, Arthisree et. al. observed a change in structural, mechanical, optical and electrical properties as a function of GQD concentration [46]. An increase in crystallinity and a decrease in direct band gap was observed with increasing GQD content, resulting in increased photoluminescence intensities with increased GQDs [46]. Shore A softness results showed a decrease with increasing GQD concentration [46]. SEM and TEM analysis showed dispersion of the GQDs in the polymer matrix, which supported the overall change in the softness results due to well distributed GQDs [46]. Gobi et. al. also showed changes in mechanical properties as a function of GQD concentration in an epoxy matrix [45]. A 225 % increase in tensile strength, compared to pure epoxy, was reported at a 2.5 weight percent concentration of GQDs [45]. Additionally, an 18 % increase to the tensile stain, despite the increase in tensile strength, and a 2.5 times increase in the Young's modulus was found with the addition of GQDs into the epoxy matrix [45]. These examples suggest the implementation of GQDs as a secondary phase addition to material systems can enhance many material properties.

All this research leaves the question, how do GQDs behave in oxides and compounds? A recently published article investigating the enhancement of photocatalytic properties when anatase TiO_2 is doped with GQDs offers some insight to the effects GQDs can have in ceramic nanocomposites [47]. By exfoliation of bird charcoal at varying temperatures, different sized GQDs were created and UV-vis

spectroscopy showed a slight red shift in the emission spectrum as a function of increasing GQD particle size [47]. Photoluminescence spectroscopy showed thermal treatment had little impact on the emission spectrum of QGDs but the highest photoluminescence intensity was found at 635 nm wavelength with an excitation at 580 nm [47]. However, doping TiO₂ with GQDs showed a dependence of GQD concentration on the photoluminescence intensity, increased doping concentration resulted in increased intensity, and it was suggested incorporation of GQDs induced more defect sites that resisted electron hole pair recombination [47]. The photocatalytic properties were conducted by degradation of methylene blue where the presence of GQDs enhanced the photocatalytic performance [47]. TiO₂ doped with 1 wt.% GQDs showed the greatest degradation with the highest calculated rate constant relative to the other doped samples and pure TiO₂ [47].

CHAPTER THREE

RESEARCH OBJECTIVE

3.1 Objective

The objective of this thesis was to investigate the processing and structure of Ce-ZrO₂ nanoparticles doped with GQDs when derived by the NaBH₄ precipitation method. Ce-ZrO₂ material systems have been researched extensively, however there appeared to be some gaps in research regarding the optimization of the materials performance with respect to synthesis routes. In addition, GQD doping has shown to enhance performance of some material systems but due to infancy of GQDs, much research was still needed. Several key publications served as guidance for the focus and development of this thesis.

3.2 Justification

Previous research has shown low temperature stabilized t-ZrO₂ nanoparticles produced by an aqueous NaBH₄ precipitation method enhanced porosity and surface area over other synthesis methods due to in-situ hydrogen gas evolution [19,20]. In addition, a coprecipitation of Ce-ZrO₂ nanocomposites, produced by a different synthesis method, showed enhancements in porosity and surface area [27]. There did not appear to be studies in the literature covering coprecipitation of Ce-ZrO₂ nanocomposites that used the NaBH₄ synthesis method, which raised the question whether NaBH₄ synthesis of Ce-ZrO₂ nanocomposites would result in additional enhancements compared to either one.

CeO₂ and ZrO₂ share some similar mechanical, thermal, and electrical properties that have been found useful in applications like polishing media, thermal barriers and fuel cells. Combination of the two have shown to enhance other properties such as catalytic

activities, which enhanced stabilization of the lattice and in turn allowed further extent of the reaction to take place [30]. With increased lattice stability during reactions when combining CeO_2 and ZrO_2 , and with increased porosity and surface area from the use of the NaBH_4 precipitation method, it was hypothesized that performance enhancements in properties like chemisorption, gas storage-production, and conductivity would be a result.

Due to the infancy of GQDs, much research still remained for the impact this relatively new material could have in applications. Research has shown enhancements to mechanical, optical, and electrical properties of polymer-based GQD composite materials [43,45,46] and ZrO_2 -based graphene composite materials [33,35]. The only published research found which offered some insight to the effect GQDs have on ceramic based systems was the enhancement of optical and catalytic properties of TiO_2 doped with GQDs [47]. From these research efforts, it was suspected GQDs could tailor optical, electrical, and chemical properties of Ce- ZrO_2 composites while enhancing structural and mechanical properties.

Using these resources to project an outcome for this thesis study, NaBH_4 derived GQD doped Ce- ZrO_2 nanocomposites could have compounded enhancements in electrical, chemical, optical, and mechanical properties. Furthermore, NaBH_4 precipitation route offers a simple and environmentally friendly synthesis process from abundantly available resources. With little to no hazardous byproducts, this synthesis route could be a viable alternative to other production methods used in commercial applications.

CHAPTER FOUR

MATERIALS AND METHODS

In order to develop this work of process and characterization of GQD doped Ce-ZrO₂ nanocomposites, several aspects were addressed. Sample preparation, experimental plan, and equipment needed were addressed in the experimental setup, apparatus and supplies sections below. The safety section covers all safety consideration, including protective equipment, lab environment, and chemical handling. The analytical instrument and data analysis section covers the tools used to collect data and the methods used to analyze the data, respectively.

4.1 Experimental Setup

Samples were produced by mixing aqueous solutions of NaBH₄ with aqueous solutions containing CeO₂, ZrO₂, and GQD precursors in a previous study. Brief, processing is as follows: a 5 molar aqueous solution of NaBH₄ was prepared by adding the appropriate volume of deionized (DI) water to the appropriate weight of solid NaBH₄ ($\geq 98.0\%$ grade), the actual volume and weight depended on the total amount of each sample needed for analysis. Three different categories of precursors were used for this study, one for pure ZrO₂, one for 16 mol % Ce-ZrO₂, and one for 16 mol % Ce-ZrO₂ containing GQDs. To study the effects functional group may have on the Ce-ZrO₂ systems, aminate and carboxylate GQDs were used. For pure ZrO₂ samples, a 0.5 molar aqueous solution of ZrO₂ was prepared by adding the appropriate volume of DI water to the appropriate weight of ZrOCl₂·8H₂O (99.5% grade). For Ce-ZrO₂ samples, a 0.5 molar aqueous solution was prepared by adding the appropriate volume of DI water to the

appropriate weight of cerium chloride heptahydrate ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ – 99.5% grade) and ZrO_2 oxychloride octahydrate. Equation 2 was used to calculate the weight of each component needed with respect to the volume of solution, where x is the mole percent of cerium projected to be in each sample. To add the GQDs, a 25 grams per liter solution of GQDs in DI water was used in substitution of the DI water described above in the CeO_2 and ZrO_2 precursors. Equation 3 was the calculation for the amount of GQD solution used when preparing the precursors, where y is the GQD concentration (in grams per liter of solution) and x is mol % of cerium projected to be in each sample.

$$\text{Ce}_x\text{Zr}_{1-x}\text{O}_2 = 1.686 \frac{\text{grams } (\text{CeCl}_3 \cdot 7\text{H}_2\text{O})}{\text{L solution}} * x + 1.611 \frac{\text{grams } (\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O})}{\text{L solution}} * (1-x) \quad \text{Equation 2}$$

$$\text{Wt.\% GQD} = \frac{y}{y + 86.059 \frac{\text{grams}}{\text{L solution}} (\text{CeO}_2) * x + 61.611 \frac{\text{grams}}{\text{L solution}} (\text{ZrO}_2) * (1-x)} \quad \text{Equation 3}$$

The synthesis process to produce the GQD-Ce- ZrO_2 nanocomposite samples is outlined in the flow diagram in Figure 12. To prepare a sample batch, a precursor solution was added dropwise to a NaBH_4 solution at room temperature. During addition of the precursor, the mixture was manually stirred vigorously to ensure thorough mixing. After stirring, the solution was left to settle the precipitate particles to the bottom of the containment, where then a transfer pipet was used to remove the bulk of the aqueous boron complex byproduct. DI water was added to the solution to dilute the boron complex, effectively rinsing the precipitated particles. The particles were allowed to settle and the bulk diluted boron complex byproduct was removed, again by a transfer pipet. These two steps, dilution with DI water and removal of the diluted boron complex byproduct, were repeated until the solution pH was that of the DI water. The rinsed precipitates were dried in an oven at 80 °C for 24 hours to remove as much moisture as

possible. Finally, the dried precipitates were ground with a pestle and mortar to form a fine powder.

GQD-Ce-ZrO₂ Nanocomposite Synthesis Flow

Figure 12. Process flow diagram to produce GQD doped Ce-ZrO₂ nanocomposites.

To achieve crystallinity of the synthesized samples, each needed to be calcined at elevated temperatures. Table 4 is the sample matrix showing the Ce-ZrO₂ composition, the GQDs content, and the various calcine temperatures. Each sample was calcined for 1 hour. Alumina crucibles were chosen for the thermal treatment because it could be easily traced to the annealing process if contamination issues were observed during chemical analysis. A KP-type thermocouple was used to calibrate and monitor the furnace temperature.

Table 4. Sample matrix for GQD weight percent concentrations and calcination temperatures.

Composition	GQD Content (wt. %)	Calcine Temperature (°C)
ZrO ₂	0	400, 500, 650, 700, and 800
ZrO ₂ with amine GQD	3 and 7	700
Ce _{0.16} Zr _{0.84} O ₂	0	700
Ce _{0.16} Zr _{0.84} O ₂ with amine GQD	0.1 and 0.5	700
Ce _{0.16} Zr _{0.84} O ₂ with carboxyl GQD	0.1 and 0.5	700

4.2 Apparatus and Supplies

Starting with synthesis of the samples, typical chemical lab equipment was needed. First and foremost, a fume hood with greater than 100 feet per minute face velocity was used for all chemical work. Glass beakers were used to contain the solutions and a scale was used to measure the quantities of the solid chemicals for each batch. Spatulas, pipets, and graduated cylinders were used to handle the solid chemicals and measure the volumes of DI water and GQD solutions. ZrOCl₂ · 8H₂O (99.5% grade), CeCl₃ · 7H₂O (99.5% grade), and NaBH₄ (≥98.0% grade) were all procured from Sigma-Aldrich. The GQD solutions were obtained from ACS Materials. A glass stirrer was used for both preparation of the precursor solutions and mixing of those solutions used to produce the precipitate particles.

To complete the synthesis process, a low temperature oven was used to dry the resulting samples. Then a pestle and mortar were used to grind the samples to a fine

powder. While the samples were ground after drying, a 3M N95 breathing mask was used for inhalation protection because this process could not be done in a fume hood.

The thermal treatment process required the use of a high temperature furnace. Thermal barrier gloves, eye protection, and long metal tongs were used for safe handling. Alumina crucibles were used to contain the samples and KB-type thermocouples were used to monitor the furnace temperature.

4.3 Safety

In the production of GQD doped Ce-ZrO₂ nanocomposites, possible touch contact and inhalation were of primary safety concerns. To address the possible touch contact risks, personal protective equipment (PPE) of goggles, gloves, and a lab coat were worn at all times during synthesis, thermal treatment, and sample analysis preparation steps. To address the inhalation safety risks, a fume hood was used during chemical handling and synthesis of the samples. During the grind to powder samples and handling while preparing for analysis, a 3M N95 particle mask was used. The safety data sheets (SDS) for each chemical was obtained from either the source it was purchased from or the manufacture of that particular chemical. The chemical hazard ratings, recommended PPE, and other safety considerations, like chemical compatibilities, obtained from each SDS are tabulated in Table 5. Since the addition of water to NaBH₄ evolves hydrogen gas, which is flammable, a fume hood was used, any non-needed ignition sources were removed from the vicinity, and an ABC fire extinguisher was available in case needed. Both eye wash and safety shower stations were confirmed to be operational before any lab work. Spill clean-up kits were confirmed to be present and properly stocked.

Table 5. Summary of hazard ratings, PPE and noteworthy information from the SDS for each chemical used in this study.

Chemical	Health Hazard Rating	Flamm- ability Rating	Reactivity Hazard Rating	PPE	Other
Zirconium Oxychloride Octahydrate	3	0	0	Gloves, Goggles, Lab coat	Incompatibility with strong oxidizing agents
Cerium Chloride Heptahydrate	2	0	0	Gloves, Goggles, Lab coat	Incompatibility with strong oxidizing agents and acids
Sodium Borohydride	3	4	2	Gloves, Goggles, Lab coat	Contact with water produces flammable gas, use fume hood
Graphene Quantum Dots	0	0	0	Gloves, Goggles, Lab coat	
Isopropyl Alcohol 99% Grade	1	3	0	Gloves, Goggles, Lab coat	Use with vapor respirator or fume hood

Touch contact and inhalation safety were also of concern during the thermal treatment process. The PPE used for this process consisted of latex gloves, goggles, and a lab coat. Since the samples were in powder form at this time a 3M N95 particle mask was used to protect against inhalation hazard. To protect against burn related risks, thermal barrier mitts and coat, face shield, and tongs were used during loading and unloading of samples in the furnaces. Each furnace used was inspected for safe operation and the main fuses were located in case power needed to be shut off in an emergency.

4.4 Analytical Instruments and Data Analysis

The various samples in this study were analyzed for their thermal events, crystalline structure, material composition, bonding states, particle morphology, and lattice parameters. The analytical techniques used to obtain this information were DSC/TGA, XRD, XPS, SEM and TEM. The experimental matrix showing the analytical techniques used for each sample composition, GQD content, and thermal treatment are outlined in Table 6.

Table 6. Experimental matrix of analytical techniques used for each sample composition, GQD content, and thermal treatment.

Composition	GQD Content (wt. %)	Calcine Temp. (°C)	DSC & TGA	XRD	XPS	SEM	TEM
ZrO ₂	0	Unannealed	√	√			
		400		√			
		500		√			
		650		√			
		700		√	√	√	√
		800		√			
ZrO ₂ with amine GQD	3	Unannealed	√				
		700		√	√	√	√
	7	Unannealed	√				
		700				√	
Ce _{0.16} Zr _{0.84} O ₂	0	Unannealed	√				
		700		√	√	√	√
Ce _{0.16} Zr _{0.84} O ₂ with amine GQD	0.1	Unannealed	√				
		700		√	√	√	√
	0.5	Unannealed	√				
		700		√	√	√	√
Ce _{0.16} Zr _{0.84} O ₂ with carboxyl GQD	0.1	Unannealed	√				
		700		√	√	√	√
	0.5	Unannealed	√				
		700		√	√	√	√

4.4.1 Thermal Analysis

DSC and TGA were conducted using a Perkin Elmer Simultaneous Thermal Analyzer STA8000 with nitrogen gas flow. The tool's specifications were 0.2 μg balance resolution, 0.5 $^{\circ}\text{C}$ temperature accuracy and 5 % calorimetric accuracy. The temperature range tested for each sample was 30-1200 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}$ per minute. Alumina crucibles were used for thermal stability throughout the tested temperature range and about 10-15 mg of each sample were used per test. Weight loss of the samples was monitored by the TGA mode where the change in the weight versus temperature was recorded. The weight loss at particular temperatures was used to identify particular thermal events such as dehydration, evaporation, and decomposition. Heat flow in the samples was monitored by the DSC mode, where the difference in heat between the sample and an empty reference crucible was recorded. The difference in heat flow between the reference and sample crucibles indicated a thermal event such as a phase transformation. The plain ZrO_2 sample was tested to serve as a base to compare with the different Ce- ZrO_2 and GQD samples. The Ce- ZrO_2 sample was tested to correlate against the GQD doped samples to observe the effect GQDs had on crystal formation and phase transformation. Each of the GQD containing samples were tested to observe any effects on crystal formation and phase transformation with respect to GQD concentration. The tests were conducted at Perkin Elmer's facility in San Jose, CA, where training and supervision was provided by Dr. Jun Wang. I conducted the tests and analysis.

4.4.2 X-Ray Diffractometry

XRD was conducted using a Rigaku Ultima III XRD with a copper $K\alpha$ radiation source operating at 40 kV and 44 mA. A scanning velocity of 6° per minute recording data at every 0.01° intervals over a range of $20 < \theta < 80^\circ$ was used with a detection limit of 1 wt. %. ICDD cards were used with MDI's Jade software to identify the observed diffraction peaks. The intensity of the diffracted x-ray beam was recorded versus the angle at which they were detected and peaks of high intensity were used to identify particular crystalline structures. XRD was also chosen to determine if CeO_2 and ZrO_2 mixed oxides were made or if coprecipitation occurred for the various samples. The PPE used were safety goggles, latex gloves, lab coat, and a 3M N95 particle mask. The tests were conducted at the MC² Metrology Center at San Jose State University. Samples were prepared and loaded by myself and scans conducted by Dr. Craig England.

4.4.3 X-Ray Photoelectron Spectroscopy

The chemical composition and bonding states were characterized by XPS using a Thermo Scientific K-Alpha system with a detection limit of 0.1-0.2 at. % equipped with an Al $K\alpha$ x-ray source under ultra-high vacuum. A $400\text{ }\mu\text{m}$ spot size was used with a take-off angle of 90 degrees and sample charging was compensated with an electron flood gun. Each sample powder was placed on a coin of indium foil and gently pressed to hold in place and flatten for analysis. The PPE used were safety goggles, latex gloves, lab coat, and a 3M N95 particle mask. The C 1s, Ce 3d, Ce 4d, Mg 1s, O 1s, Zr 3d, and Zr 3p core levels were recorded for each sample. All samples annealed at 700°C were analyzed using this spectroscopy technique. Each sample composition was obtained and

compared to the expected theoretical composition, outlined in Equation 2 and Equation 3. The XPS tests were conducted at Nanolab Technologies facility in Milpitas, CA, where sample preparation and analysis was conducted by Dr. Jeff Gold.

4.4.4 Scanning Electron Microscopy

Particle morphology was studied using a FEI Nova NanoSEM 630 equipped with a field emission electron gun at or lower than 5 kV with a resolution of 1.6 nm. For sample preparation, the PPE used were safety goggles, latex gloves, lab coat, and a 3M N95 particle mask. The powder samples were diluted in Isopropyl Alcohol (IPA) and sonicated for 30 minutes to further disperse the particles. Then a pipet was used to place a drop on a sample stub which then was placed under a heat lamp to evaporate the IPA. SEM images were obtained as data from this analysis and used to characterize particle morphology, particle size, and degree of agglomeration. SEM inspection was conducted at Nanolab Technologies facility in Milpitas, CA, where I prepared and analyzed the samples.

4.4.5 Transmission Electron Microscopy

TEM analysis was done at two different facilities. The first facility was Nanolab Technologies in Milpitas, CA where a JOEL 2100 High Resolution Transmission Electron Microscope (HRTEM) operating at 200 kV with a 0.8 nm resolution was used. The second facility was EAG Laboratories in Sunnyvale, CA where a FEI Tecnai TF-20 FEG/TEM operating at 200 kV with a 0.6 nm resolution was used. Bright-Field (BF), High-Resolution (HR), and High-Angle Annular Dark-Field (HAADF) Scanning TEM (STEM) modes were used. For sample preparation, the PPE used were safety goggles,

latex gloves, lab coat, and a 3M N95 particle mask. Similar to the SEM sample preparation, each sample was diluted in IPA, sonicated for 30 minutes, and a drop was placed on a copper grid coated with a holey carbon film and dried under a heat lamp. TEM images and diffraction patterns were obtained as data from this analysis and used to characterize particle size, nanostructures, atom and lattice distances, and presence of GQDs. The images were analyzed using Digital Micrograph version 3.22 and atom to atom distances were measured and compared to theoretical values. The theoretical values were calculated from Vegard's Law, shown in Equation 4, where A represents CeO₂, B represents ZrO₂, x represents the mole percent of cerium, and a is the lattice parameter in angstroms.

$$a_{AxB(1-x)} = (x)a_A + (1 - x)a_B \quad \text{Equation 4}$$

In addition to microscopy with TEM, chemical analysis was conducted using a Tecnai ChemiSTEM EDS with a detection limit of 1 at. % on the FEI TEM. The EDS analysis was processed with Bruker Quantax software. Sample preparation was completed by myself and operation of the TEM and image acquisition was done by Dr. Zhou Yang at Nanolab Technologies and Yulia Grozman at EAG Laboratories.

CHAPTER FIVE

RESULTS AND DISCUSSION

5.1 Thermal Analysis

The DSC and TGA curves showed the release of physically absorbed water, released hydroxyl (OH^-) groups, and the crystallization for each sample. The DSC and TGA curves for samples ZrO_2 , Ce-ZrO_2 , Ce-ZrO_2 with amine GQDs, and Ce-ZrO_2 with carboxyl GQDs, both containing 0.5 wt. % GQDs, are represented in Figure 13 and Figure 14, respectively. The first peak, endothermic, shown in the DSC curves of Figure 13 occurred between 63 °C and 73 °C, which represented the release of physically absorbed water. The first TGA weight loss step, correlating to the first DSC peak, seen in Figure 14 ranged approximately 6 to 9 wt. % confirmed the desorption of physically absorbed water. The second peak, endothermic, seen in the DSC curves occurred between approximately 188 °C and 258 °C and correlated with the second TGA weight loss step (Figure 14). In addition to the continuation of water desorption, this second weight loss step represented the removal of OH^- groups, forming ZrO_2 from $\text{Zr}(\text{OH})_4$. The third DSC peak, exothermic, occurred between approximately 660 °C and 717 °C and correlated with the third weight loss step in the TGA curves. The third peak represents the crystallization of the ZrO_2 matrix and will be further explained in the next section.

Table 7 tabulates the weight loss percent for each TGA step and the DSC peak temperatures for ZrO_2 , Ce-ZrO_2 , and both amine and carboxyl GQD doped samples with both 0.1 and 0.5 wt. % content. The addition of CeO_2 to ZrO_2 reduced the overall

amount of weight loss, as seen in Figure 14. The presence of CeO₂ or GQDs did not appear to influence the amount of physically absorbed water or the amount of OH⁻ groups released during heating. For example, the Ce-ZrO₂ sample showed a higher desorption of water than the ZrO₂ sample during the first TGA step, whereas all other samples containing CeO₂ desorbed less water with the exception of 0.5 wt. % amine GQD doped Ce-ZrO₂ sample, which was similar to the ZrO₂ sample. The same lack of trend amongst all samples and their associated weight loss stages suggested either dopants are independent of weight loss or there was a lack of control during the synthesis process. The former is less likely when absorption/desorption has been shown to be influenced by dopants in ZrO₂ systems [31]. Both the first and second DSC endothermic peaks correlating to the first and second weight loss steps did not show a trend between samples, nor appear influenced significantly by primary or secondary dopants. However, the most notable dopant dependency on thermal events was during crystallization, the exothermic event in the third DSC peak. The presence of CeO₂ affected the onset of crystallization, indicated by the arrow in Figure 13 at the lower temperature values at the exothermic peaks. The addition of CeO₂ reduced the crystallization temperature by about 40 °C, from 700 °C for ZrO₂ to about 660 °C for all samples except the 0.1 wt. % amine and carboxyl GQD doped samples. The lowering of the transformation temperature with CeO₂ doping is in agreement with others findings [27,51,52] and the discrepancy with the 0.1 wt. % GQD doped samples was believed to be due to low synthesis control. The presence of GQDs did not appear to affect the weight loss trend or phase transformation.

Figure 13. Normalized DSC results for ZrO₂, Ce-ZrO₂, 0.5 wt. % amine GQD-Ce-ZrO₂, and 0.5 wt. % carboxyl GQD-Ce-ZrO₂ samples.

Figure 14. TGA weight loss percent results for ZrO₂, Ce-ZrO₂, 0.5 wt. % amine GQD-Ce-ZrO₂, and 0.5 wt. % carboxyl GQD-Ce-ZrO₂ samples.

Table 7. TGA weight loss steps and DSC events peaks tabulated for ZrO₂, Ce-ZrO₂, and Ce-ZrO₂ samples doped with either amine or carboxyl GQDs at both 0.1 and 0.5 wt. %.

Sample	TGA Weight Loss (wt. %)			DSC Event Peaks (°C)		
	Step 1	Step 2	Step 3	Peak 1	Peak 2	Peak 3
ZrO ₂	8.035	6.694	0.671	65.42	188.35	701.88
Ce _{0.16} Zr _{0.84} O ₂	9.066	2.742	0.109	68.88	257.56	661.88
Ce _{0.16} Zr _{0.84} O ₂ with 0.1 wt. % amine GQD	7.752	6.453	0.542	87.23	207.27	716.64
Ce _{0.16} Zr _{0.84} O ₂ with 0.1 wt. % carboxyl GQD	7.166	6.370	1.501	61.12	194.99	705.58
Ce _{0.16} Zr _{0.84} O ₂ with 0.5 wt. % amine GQD	8.195	3.749	0.247	67.93	241.33	666.89
Ce _{0.16} Zr _{0.84} O ₂ with 0.5 wt. % carboxyl GQD	6.695	3.432	0.294	72.69	239.44	666.61

5.2 Crystallographic Analysis

In addition to observing the crystalline transition with increasing temperature, XRD was used to confirm the tetragonal crystalline phase after thermal treatment for all the doped ZrO₂ samples. Figure 15 shows the increase in crystallinity for pure ZrO₂ annealed at 400 °C, 600 °C and 700 °C, where amorphous to tetragonal crystalline structure was observed. Both 400 °C and 600 °C showed no significant peaks indicating amorphous structure. However, 700 °C showed clear crystalline peaks that correlate to t-ZrO₂ crystalline structure. To observe any phase dependency on doping of ZrO₂, XRD was performed on all samples. Results for the ZrO₂, Ce-ZrO₂, Ce-ZrO₂ with amine or carboxyl GQDs, containing either 0.1 or 0.5 wt. % GQDs are represented in Figure 16.

The XRD analysis confirmed t-ZrO₂ crystalline structure for all samples annealed at 700 °C. The crystallite size and lattice parameters are tabulated in Table 8 showing the addition of Ce reduced the crystallite size and increased the interplanar spacing. This was due to the larger ionic radius of cerium (0.097 nm) compared to zirconium (0.084 nm), resulting in stretching the lattice structure and suppressing the crystalline growth. This observation was in agreement with other research [49]. Pure ZrO₂ had a crystal size of approximately 19 nm, whereas all samples containing Ce were approximately 15 nm in size. There did not appear to be any discernible effects from the presence of GQDs.

Figure 15. Onset of crystallinity with increased annealing temperature of ZrO₂ by XRD.

Figure 16. XRD intensity peaks for ZrO_2 , Ce-ZrO_2 , Ce-ZrO_2 with amine GQDs or carboxyl GQDs, containing either 0.1 or 0.5 wt. % GQDs, all annealed at 700 °C.

Table 8. Lattice parameter values tabulated for samples calcined at 700 °C.

Samples	Crystallite Size (nm)	Experimental Lattice Parameters	
		a=b (Å)	c (Å)
ZrO_2	19.4±0.4	3.596	5.138
Ce-ZrO_2	14.6±0.3	3.635	5.227
0.1 wt. % amine GQD- Ce-ZrO_2	15.4±0.3	3.637	5.227
0.1 wt. % carboxyl GQD- Ce-ZrO_2	14.8±0.3	3.636	5.229
0.5 wt. % amine GQD- Ce-ZrO_2	14.3±0.3	3.636	5.228
0.5 wt. % carboxyl GQD- Ce-ZrO_2	15.0±0.3	3.635	5.226

5.3 Compositional Analysis

XPS analysis for all samples revealed the concentration of Ce to be 13-14 at. % for each sample, 2-3 at. % lower than targeted 16 at. % Ce for the precipitation reaction. Table 9 covers ZrO₂, Ce-ZrO₂, and Ce-ZrO₂ samples doped with either amine or carboxyl GQDs at both 0.1 and 0.5 wt. %. Trace sodium and magnesium were detected and were attributed to be remanence from the synthesis process or contamination during annealing or sample preparation. The presence of GQDs did not show any significant impact on the stoichiometry of the composite samples. There was no consistent elevation of carbon detected by XPS with the samples containing GQDs, nor between samples with increased GQD concentration. XPS did not offer conclusive evidence to the presence of GQDs remaining after synthesis.

Table 9. Compositional and Ce-ZrO₂ ratio results from XPS analysis.

Sample	<u>Composition (at. %)</u>						Ce /CeZr (%)
	Ce 3d	Zr 3d	O 1s	C 1s	Na 1s	Mg 1s	
ZrO ₂	0.0	17.1	82.0	0.4	0.0	0.4	0.0
Ce-ZrO ₂	2.4	15.6	81.4	0.6	0.0	0.1	13.3
0.1 wt. % amine GQD-Ce-ZrO ₂	2.4	15.6	81.9	0.0	0.1	0.0	13.3
0.1 wt. % carboxyl GQD-Ce-ZrO ₂	2.5	15.6	81.6	0.2	0.0	0.0	13.8
0.5 wt. % amine GQD-Ce-ZrO ₂	2.4	15.6	81.3	0.5	0.0	0.2	13.3
0.5 wt. % carboxyl GQD-Ce-ZrO ₂	2.6	16.3	80.3	0.6	0.0	0.2	13.8

EDS with a TEM was also performed on the 0.5 wt. % amine GQD-Ce-ZrO₂ sample calcined at 400 °C to possibly detect the presence of GQDs at a lower annealing temperature. Figure 17 shows the presence of Ce-based crystalline particles along with amorphous Zr-based particles. The EDS analysis showed individual crystalline CeO₂ particles among an amorphous ZrO₂ matrix. The crystallinity of the CeO₂ was not detected in either DSC or XRD analysis. DSC did not exhibit an exothermic reaction below 400 °C nor did XRD show crystalline peaks within samples annealed at 400 °C. More TEM investigations are needed to fully characterize the structures of GQD-Ce-ZrO₂ nanocomposites and reveal the phase changes with annealing temperature.

Figure 17. HAADF TEM and EDS mapping images of separate Ce-based agglomerated particles for 0.5 wt. % amine GQD-Ce-ZrO₂ sample calcined at 400 °C.

5.4 Morphology and Structural Analysis

The particle morphology of samples (a) ZrO₂, (b) Ce-ZrO₂, (c) 0.5 wt. % amine GQD-Ce-ZrO₂, and (d) 0.5 wt. % carboxyl GQD-Ce-ZrO₂ are illustrated in the SEM micrographs of Figure 18. Samples containing CeO₂ appear to have larger extent of

particle agglomeration than plain ZrO_2 , whereas samples with GQDs do not appear to have any observable effects on the morphology. Larger agglomeration may contribute to the larger weight loss in the first TGA step, resulting from a larger release of physically retained water. The average particle size for all samples ranged between of 20-35 nm.

Figure 18. High Resolution SEM (HRSEM) micrographs showing particle morphology of (a) ZrO_2 , (b) CeZrO_2 , and CeZrO_2 with (c) 0.5 wt.% amine GQDs and (d) 0.5 wt.% carboxyl GQDs.

TEM micrographs of (a) ZrO_2 , (b) Ce-ZrO_2 , (c) 0.1 wt. % amine GQD- Ce-ZrO_2 , and (d) 0.5 wt. % amine GQD- Ce-ZrO_2 are shown in Figure 19. Lattice measurements from the electron diffraction patterns, inserts in each image, are in approximate agreement with XRD lattice parameter measurements. It was extremely difficult to tell but lattice and particle measurements suggested GQDs were observed in some samples. Figure 20 suggests the presence of GQDs for the 0.5 wt. % amine GQD- Ce-ZrO_2 sample (a) unannealed and (b) annealed at 700 °C. The lattice parameter measurements of 0.319 nm

and 0.304 nm are close to the theoretical 0.33 nm GQD basal plane. The original size of the GQDs were ~10 nm or smaller and the particles in Figure 20 are also about 10 nm or less. Further study and reduction of agglomeration are needed to understand the functional attachment of the GQDs to the ZrO₂-based matrix.

Figure 19. HRTEM micrographs showing diffraction patterns and lattice measurements for (a) ZrO₂, (b) Ce-ZrO₂, (c) 0.1 wt. % amine GQD-Ce-ZrO₂ (d) 0.5 wt.% amine GQD-Ce-ZrO₂.

Figure 20. HRTEM micrographs of the (a) 0.5 wt. % amine GQD-Ce-ZrO₂ sample unannealed and of the (b) 0.5 wt. % amine GQD-Ce-ZrO₂ annealed at 700 °C.

CHAPTER SIX

CONCLUSION

In this study, previous NaBH_4 precipitated Ce- ZrO_2 was characterized for effects amine and carboxyl GQDs may have on the phase and morphology of Ce- ZrO_2 nanoparticles. DSC and TGA analysis showed the evolution of Zr(OH)_4 to crystalline ZrO_2 when heating past 700 °C through dehydration, release of OH^- groups, and crystallization. XRD analysis confirmed the evolution of amorphous to tetragonal phase transformation for resulted ZrO_2 -based nanoparticles. The presence of CeO_2 reduced the amorphous-to-tetragonal transformation temperature by ~40 °C and reduced the average crystallite size from approximately 19 nm for ZrO_2 to approximately 15 nm for Ce- ZrO_2 . There was no discernible effect GQDs had on the crystallinity of the Ce- ZrO_2 structure. XPS compositional analysis revealed 13-14 at. % CeO_2 in the ZrO_2 matrix, despite the targeted 16 at. %.

More TEM work is needed to conclude the presence of the GQDs in the ZrO_2 systems and the effects they may have on the Ce- ZrO_2 structure. Future studies should focus on sintering of the GQD-Ce- ZrO_2 system and characterization of the sintered nanocomposite. The GQDs may survive the sintering process or might produce nanopores. These structures, in turn, could improve toughness of ZrO_2 by enhancing transformation toughening or microcrack formation at the crack tip [53].

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