

Defect Engineering in Cerium Oxide Nanocrystals: From Catalyst to Quantum Bit

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Abstract

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Nanocrystalline CeO_2 (ceria) is a versatile material that plays a critical role in a wide range of applications from biotechnology and heterogeneous catalysis to quantum information, due to its ability to host a variety of defects and dopants within its crystalline lattice. In this dissertation, we will explore the multifaceted properties of CeO_2 and how to manipulate its structure to modulate its function in two different applications: heterogeneous catalysis and quantum information technology.

In Chapter 1, we lay out the rich body of studies that elucidate ceria's structure and function across multiple contexts. We explore what it means to "defect engineer" ceria by introducing dopants to produce an effective heterogeneous catalyst. Then, we discuss the rapidly growing field of quantum information technology, focusing on the emerging interest in ceria as a host lattice for quantum bits, and consider reverse-engineering ceria to generate a defect-free environment. Finally, we provide context for where that positions this dissertation in our effort to contribute knowledge to the field of nanocrystalline cerium oxide.

In Chapter 2, we introduce the context for CeO_2 nanocrystals and their applications in organophosphate hydrolysis. We unpack the uncertainties in the literature regarding the relationship between specific surface

defects and catalytic activity in dephosphorylation. Trivalent dopants serve as a tool for manipulating defects, including the concentration of Ce^{3+} and oxygen vacancies, thereby influencing the hydrolytic activity of CeO_2 . By studying the catalytic degradation of dimethyl-*p*-nitrophenyl phosphate (DMNP) as a model organophosphate substrate with doped CeO_2 and piecing together a picture of the catalytic surface by powder X-ray diffraction (PXRD), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy, we show that CeO_2 exhibits high sensitivity to dopants that generate lattice strain, Ce^{3+} ions, and oxygen vacancy defects. Consequently, we postulate that achieving high catalytic efficiency in CeO_2 requires a balanced active site ensemble, in which defects are maintained at optimal concentrations and distributions on the nanocrystal surface.

In Chapter 3, we reframe CeO_2 as a chemically tunable wide-bandgap host lattice for its ability to accommodate optically active and spin-active defects. We investigate CeO_2 nanocrystals as hosts for near-infrared-compatible Yb^{3+} ions as optically active spin quantum bits (qubits), by characterizing the as-synthesized Yb^{3+} -doped CeO_2 nanocrystals (0.01–10% Yb) by photoluminescence and EPR. Thermal annealing at 700 °C increases crystalline domain sizes (from ~7 nm to ~20 nm) and reduces the concentration of Ce^{3+} defects, yielding an enhancement in excited-state lifetimes and spin-lattice relaxation time (T_1), while phase memory times don't significantly change, suggesting ulterior dephasing mechanisms not addressed by annealing. Collectively, these results establish defect mitigation, rather than dopant identity alone, as a bottleneck in realizing nanocrystalline CeO_2 as a viable quantum host. Through this work, we provide quantitative benchmarks for optical and spin coherence in $\text{CeO}_2\text{:Yb}^{3+}$ nanocrystals and highlight defect engineering as a critical pathway toward scalable rare earth-based qubits.

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DEDICATION

To Sayuri and Mark, for always being there for me

Chapter 1.

Introduction to Cerium Oxide Nanocrystals

This chapter aims to provide the scientific context for the work presented in this dissertation focused on cerium oxide nanocrystals (NCs) with an eye towards their applications in catalysis and quantum information science. To establish this foundation, Section 1.1 first explores the structure, properties, and defects of cerium oxide as they are relevant to the following chapters. Section 1.2 provides additional framing on the use of cerium oxide nanomaterials in catalysis, which will be relevant to Chapter 2. Section 1.3 discusses cerium oxide as an emerging material host for defects relevant to quantum information systems to contextualize Chapter 3. Finally, Section 1.4 will discuss the general concepts of synthesizing cerium oxide relevant to the discussions in Chapters 2–3 and Appendix A.

1.1 Cerium Oxide Structure and Properties

Rare earth oxides are of great interest to the scientific community due to their unique electronic and catalytic properties derived from having valence $4f$ orbital electrons shielded from the atom's environment by $4d$ and $5p$ electrons, unlike main group or transition metal oxides. Among these rare earth elements, cerium is the most common, approximately 0.0046 wt % of the Earth's crust, making it slightly more abundant than copper or tin.^{1,2} Because of its relative abundance compared to other rare earths and its excellent physical and chemical properties as an oxide (CeO_2 or ceria), it has gained significant traction for use in catalysis and biological applications as discussed in Section 1.2. In brief, the fields of heterogeneous catalysis include three-way catalysts (TWCs),³ solid-oxide fuel cells (SOFCs),⁴ and other redox transformations.^{1,5} In the field of biology, ceria is used in biomedicine^{6,7,8} and for biologically relevant reactions.^{9,10} Before we dive into the details of ceria's applications, the goal of Section 1.1 is to provide a

succinct summary of the pertinent properties of ceria-based materials with regard to physical, electronic, and defect structure and the trends they follow from the bulk to the nanoscale.

1.1.1 Structural Properties

Cerium oxide forms into two common phases depending on the oxidation state of Ce (III or IV, also written as Ce^{3+} and Ce^{4+}), yielding either Ce_2O_3 or CeO_2 in their stoichiometric forms. The formation of these compositions from Ce metal is spontaneous, $\Delta G_{298}^0 = -1796$ and $-1089 \text{ kJ mol}^{-1}$ per mole Ce_2O_3 and CeO_2 , respectively.^{1,11} CeO_2 , the phase of interest for the work herein, has a fluorite structure with a face-centered cubic unit cell of the space group $Fm\bar{3}m$ and a lattice constant of 5.41 Å. This unit cell structure is pictured in **Figure 1.1A**, but it's often easier to imagine the main motif as a cube with a central cerium cation around which eight equivalent oxygen anions are coordinated at the corners of the cube. Each oxygen anion is thus coordinated by four cations in a tetrahedron. As the crystalline domain reduces from bulk to nanoscale, there is an observed increase in the lattice parameter from 5.41 to 5.56 Å to reduce lattice strain (note: the lattice parameter reporting 5.56 Å is quite high and correlates to $\sim 3 \text{ nm}$ particles,^{12,13} from bulk to particles $\sim 5\text{--}6 \text{ nm}$ in size, a lattice parameter increase of 0.02–0.03 Å is usually observed, around 5.43 Å).^{14,15}

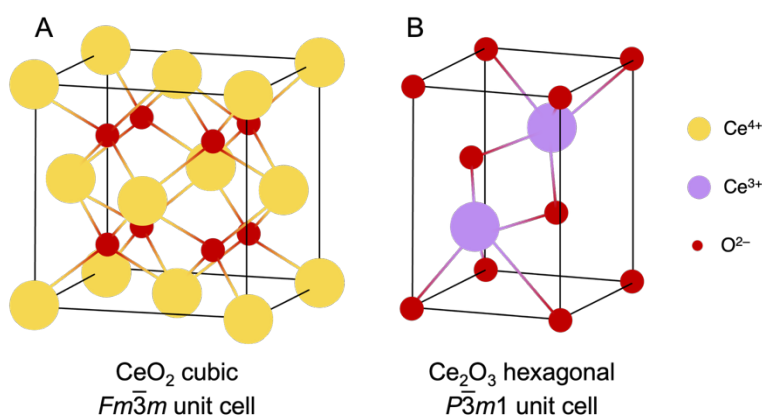
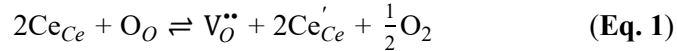


Figure 1.1. (A) CeO_2 fluorite structure with $Fm\bar{3}m$ space group unit cell and (B) Ce_2O_3 hexagonal structure with $P\bar{3}m1$ space group.

Although it is written as stoichiometric CeO₂ in many contexts, CeO₂ is often non-stoichiometric (CeO_{2-x}), as it typically contains a mixture of Ce³⁺ and Ce⁴⁺ regardless of synthesis method.¹⁵ This mixture of oxidation states within its lattice is compensated by readily releasing oxygen from the Ce coordination sphere and formation of oxygen vacancies, or in some cases, asymmetric vacancies or Frenkel-type oxygen defects,^{16,17} within the crystal structure.^{18,19} Furthermore, these sub-stoichiometric phases of CeO₂ can be associated with varying color changes to indicate the degree of sub-stoichiometry, ranging from pale yellow to blue-black.^{20,21} The formation of non-stoichiometric CeO₂ is most commonly expressed by the Kröger–Vink notation (**Eq. 1**) shown below, where Ce'_{Ce} refers to Ce³⁺, Ce_{Ce} refers to Ce⁴⁺, O_O refers to lattice oxygen, and V_O^{••} refers to a doubly ionized oxygen vacancy:²²



Many oxygen-deficient phases of CeO₂ have been identified and mapped on a Ce₂O₃–CeO₂ phase diagram, and are characterized by the ordered arrangement of oxygen vacancies with the general formula Ce_nO_{2n-2m}, such as Ce₆O₁₁, Ce₇O₁₂ and Ce₁₁O₂₀.^{1,11,21,23,24,25} Ce₂O₃ can be derived from CeO₂ when it is heated to a moderate 623 K under a reducing atmosphere of H₂, emphasizing the facile release of O²⁻ anions and subsequent reduction of Ce⁴⁺ to Ce³⁺. The reduction of ceria starts as low as 473 K but is limited to only the surface (note: at the nanoscale, the surface becomes the majority of the material).²⁶ Luckily, Ce₂O₃ is easily differentiated from CeO₂ by X-ray diffraction because Ce₂O₃ is a hexagonal lattice with a $P\bar{3}m1$ space group (**Figure 1.1B**). It is important to note that a common observation in the literature is that as the cerium oxide particle size decreases from bulk to nanosized domains, there is a corresponding increase in the Ce³⁺ concentration.¹⁵ This also provides further justification for the aforementioned lattice parameter expansion that is observed at smaller particle sizes: with the Ce³⁺ ionic radius sitting at 1.14 Å compared to Ce(IV) at 0.97 Å.¹⁴ Curiously, due to this change in the surface of the particle as the formal oxidation states of the atoms shift at smaller particle sizes, it has been proposed that cerium oxide particles are actually “core–shell” nanostructures where for relatively larger particles, the core has a stoichiometric composition of CeO₂ while the surface is closer to Ce₂O₃, however the “surface layer” thickness largely varies.¹⁵ X-ray

photoelectron spectroscopy and X-ray absorption near edge spectroscopy studies of the Ce_2O_3 thickness layer in varying CeO_2 particle sizes pointed to a 1–2 Å layer on the surface.²⁷ In response to this proposed “core–shell” description, I will point out that even in the presence of a high concentration of Ce^{3+} , the X-ray diffraction pattern of nanostructured CeO_2 often reflects a pure CeO_2 fluorite crystalline phase, suggesting no crystalline lattices of Ce_2O_3 (**Figure 1.2**).

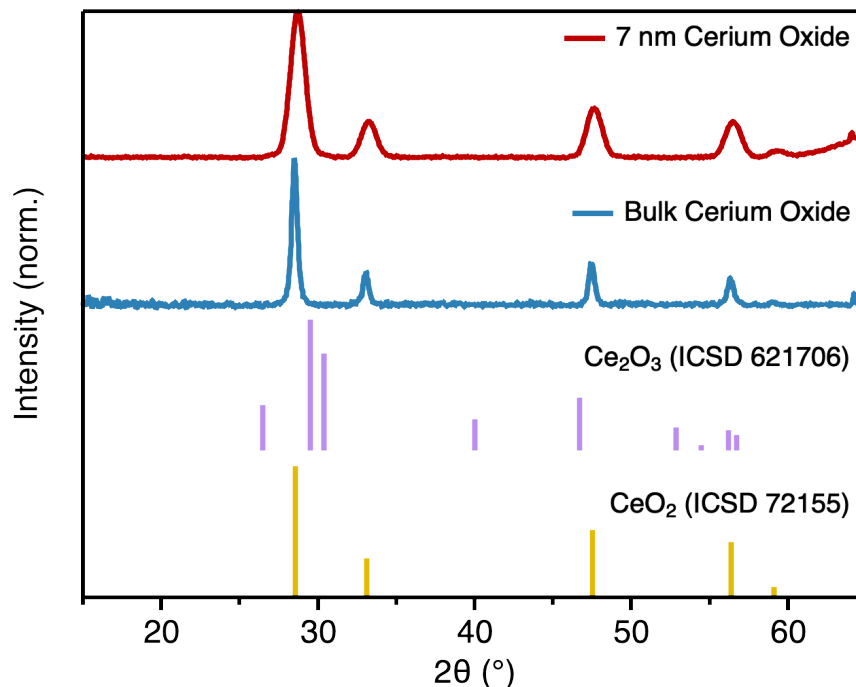


Figure 1.2. X-ray diffraction (XRD) patterns of nanocrystalline CeO_2 (~7 nm) in red, bulk CeO_2 in blue, and the reference XRD patterns for CeO_2 (ICSD 72155)²⁸ and Ce_2O_3 (ICSD 621706)²⁹ showing that both bulk and nanostructured CeO_2 reflects CeO_2 with no crystalline lattices of Ce_2O_3 .

Within the discussion of structural properties of CeO_2 , it must also be mentioned that the literature has demonstrated that CeO_2 is able to form solid solutions with a large variety of oxides. The definition of “solid solutions” is described using Vegard’s rule, where the lattice parameter is to have a linear dependence on the solute concentration incorporated into the CeO_2 matrix, although some deviations do exist.^{30,31,32} For CeO_2 specifically, an empirical relation between the lattice parameter of the solid solution and the ionic radius of a dopant dissolved in CeO_2 has been explicitly reported.³⁰ Additionally, it is believed that the

solubility of a secondary oxide into ceria is limited by the ionic radius and charge of the secondary oxide.³⁰ We discuss the structural implications of solid solutions in greater detail in Section 1.2 as they relate to applications of ceria, particularly the investigation of three-way catalysts and solid-oxide fuel cells (SOFCs).

1.1.2 Electronic Properties

Cerium oxide has several characteristic absorption features to indicate its electronic structure. There is an absorption band at 250–265 nm assigned as the charge transfer from O^{2-} to Ce^{3+} and an absorption band at 275–295 nm assigned to a ligand to metal charge transfer from O^{2-} to Ce^{4+} .^{33,34} Finally, there are reports of an absorption band at 588–650 nm, assigned to the charge transfer from Ce^{3+} to Ce^{4+} .^{33,35} One of the earliest analyses of colloidal CeO_2 particles (2.6–4.1 nm) demonstrated that as particle size decreased from 4.1 nm to 2.6 nm, the band gap energy, E_g , increased from 3.38 to 3.44 eV for direct transition and from 2.73 to 2.87 eV for indirect transition.³⁶ However, subsequent studies to correlate the relationship between band gap energy across the nanoscale are somewhat contradictory,¹⁵ as other studies observe varying values for E_g (e.g. from ~3.3 eV for 6.5 nm particles (approaching bulk values), to ~3.8 eV for 3 nm particles) and as it stands currently, an analytical relationship between absorption feature wavelength and particle size is not reliable.³⁷ In general though, the literature seems to agree that the band gap energy E_g shifts from 3.15–3.20 eV in the bulk to 3.35–3.40 eV for 3 nm particles.³⁸ On a further note, the discrepancies between multiple studies on the measured E_g to nanoparticle size is also due to a CeO_{2-x} stoichiometry, where the partial reduction of Ce^{4+} to Ce^{3+} increases the energy difference in the O $2p$ orbitals and the Ce $4f$ orbitals corresponding to a blue shift of the absorption band.³⁹

Despite a 3 or 4 eV band gap nearing the cusp of an insulator (for which E_g is typically 3–4 eV),⁴⁰ there is general agreement that CeO_{2-x} is in fact an n-type semiconductor between 200 °C and 1300 °C and that the conductivity takes place via small polaron transport.^{21,41,42,43,44} Small polaron transport is described as a defect created when an electronic carrier (such as an electron or electron hole) becomes trapped at a given site as a consequence of the displacement of adjacent atoms or ions wherein the entire defect (carrier plus distortion) then migrates by thermally activated hopping.^{21,44} They tend form in narrow bands as a result of

conduction electrons lying in incomplete inner d or f shells with small orbital overlap.⁴⁴ In the case of CeO_{2-x} , the polaron may be Ce^{3+} ions and its activation energy correlates both to electron mobility as well as electronic conductivity of the material as a whole, with a dependence on the partial pressure of oxygen.²¹ Additionally, comparisons of single crystal CeO_2 and polycrystalline samples suggest that the conductivity is not hampered by grain boundaries and that activation energy of electron hopping is similar to that of the bulk material.⁴⁵ Conversely, electron hole conductivity has only been observed under very extreme conduction of pure ceria at high partial pressures of oxygen.^{21,46}

1.1.3 Defect Structure and Redox Properties

It was demonstrated early on in our understanding of cerium oxide defects that oxygen vacancies are the predominant atomic point defects in sub-stoichiometric ceria over cation displacements within the lattice by neutron scattering studies,^{47,48} and that they can present as Frenkel-type oxygen defects (where oxygen ions occupy interstitial sites, including weakly bound oxygen that may account for the oxygen storage capacity in ceria, discussed later).¹⁶ The energetic cost to form these oxygen vacancies is also relatively low, motivating its relevance as a catalyst for redox reactions.⁴⁹

In an attempt to further improve our understanding of the CeO_2 defect structure, a computational study suggested that in the case of Ce^{3+} and other divalent and trivalent metal cations (Pd^{2+} , Pt^{3+} , and Rh^{3+}) there is local defect ordering or clustering of the defects to form a neutral cluster.⁵⁰ The defects favor the (110) surface plane, consisting of equivalent ratio of cations and anions, over the (111) surface, which is terminated by an anion-rich layer. It is rationalized that the stabilization of these defects would lie along the same surface plane on the (110) surface, whereas the (111) surface cluster would require impurities to lie within the first layer of cations, while the charge-compensating oxygen vacancies reside on the surface layer.⁵⁰ Moreover, the electrostatically-driven segregation energies (differences between the bulk and surface energies) are larger for M^{2+} cations than M^{3+} cations, and the ionic radius is also a factor in segregation energy given the reduction of elastic strain (Rh^{3+} being smaller than Ce^{4+} as opposed to Ce^{3+} having a lower segregation energy). Of course, the size of the defect clusters matters as well; larger clusters

favor the surface of the material rather than the bulk, and the surface favors smaller, more dispersed clusters over larger clusters to reduce steric strain and maximize surface relaxation.⁵⁰

Less than a decade later, computational theory was supported by experimental evidence in the form of scanning tunneling microscopy (STM) on a ceria surface, albeit on only the (111) surface and not the (110) surface. The authors demonstrated the formation of vacancy clusters on the CeO₂(111) surface, with surface oxygen vacancies and a sublayer of exposed Ce³⁺ to charge-compensate and form a neutral cluster (**Figure 1.3A**).^{51,52}

Finally, recall the note on weakly bound oxygen: computational modeling suggested four types of interactions between O₂ and a fully oxidized CeO₂(111) surface: end-on, side-on, planar bridging, and nonplanar bridging.⁵³ In the presence of sub-stoichiometric cerium oxide, O₂ appeared to favor oxygen vacancy sites by both side-on and end-on attachment, followed by Ce³⁺ adsorption over Ce⁴⁺ (**Figure 1.3B**). Their migration through a sub-stoichiometric lattice is also readily observed, where a higher fraction of oxygen vacancies correlates with lower diffusion energy barriers.⁵³

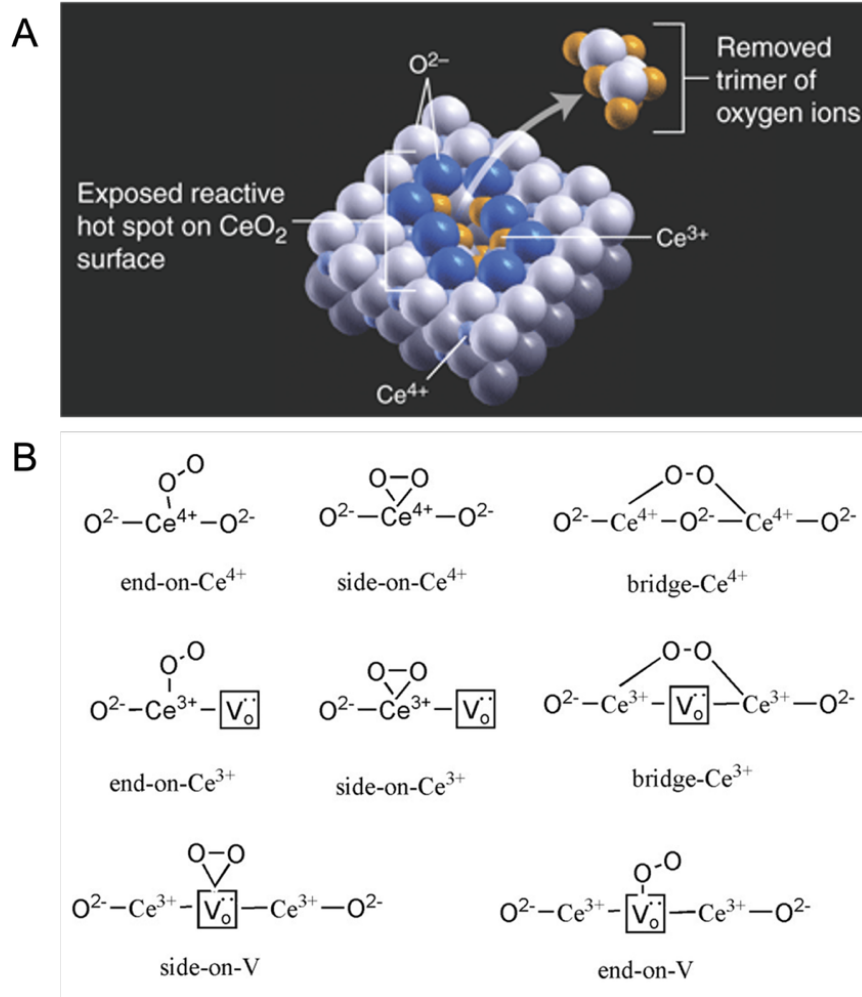
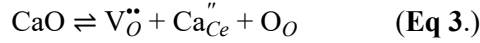


Figure 1.3. (A) Schematic depiction of reactive defect in a ceria surface showing reduced Ce³⁺ in a cluster near an surface vacancy (trimer of oxygen atoms is removed) used with permission from Ref 52. (B) Possible coordination configurations of adsorbed O₂ molecule to Ce⁴⁺ surface sites and Ce³⁺ with oxygen vacancy sites used with permission from Ref 53.

A common strategy to engineer CeO₂ defects is by using dopants to tune the relative concentrations of Ce³⁺ and oxygen vacancies, which are intrinsically related and will be affected by the incorporation of different valency dopants. As discussed previously, the oxygen vacancy defects in CeO₂ can be described by the Kröger–Vink notation. Not only the reduction of ceria compensated by oxygen vacancies as written above, but also the introduction of dopant metals of lower valencies, for example, gadolinium (**Eq. 2**) and

calcium (**Eq. 3**) shown below,²¹ where Gd'_{Ce} refers to Gd^{3+} cation neighboring a Ce atom, Ca''_{Ce} refers to a Ca^{2+} cation neighboring a Ce atom, O_O refers to lattice oxygen, and $V_O^{\bullet\bullet}$ refers to oxygen vacancies:



And oxide vacancies may be removed by doping with oxides of higher valencies such as niobium (**Eq. 4**),²¹ where $Nb^{\bullet}_{Ce}$ refers to Nb^{5+} :



The mixed oxidation states available via Ce or other extrinsic dopants, in addition to modulating the presence of oxygen atoms, are also able to impact the oxygen vacancy formation energies, thereby influencing oxygen atom adsorption and diffusion through the lattice.^{54,49} Specifically, it is suggested that isovalent nonreducible dopants (e.g. Zr^{4+}) lower defect formation energy due to a difference in ionic radius size, whereas trivalent cations (e.g. La^{3+}) create $O^{\bullet-}$ oxygen radical species that are easier to remove due to electrostatic effects, yielding a lower oxygen vacancy formation energy. In both cases, dopants are effective in stabilizing these defect formations as compared to oxygen vacancy formation in pristine CeO_2 .⁴⁹

At the nanoscale, the decrease in particle size and subsequent increase in surface area is also impacting the defects that arise within the crystals due to a more strained and faceted surface. Additionally, the various morphologies of ceria nanostructures have been shown to correlate to the relative ratios of Ce^{3+}/Ce^{4+} based on the lattice planes that are exposed, meaning that Ce^{3+} defects might be engineered via morphological control.^{55,56}

1.2 Common Cerium Oxide Applications: Catalysis

Several applications of cerium oxide have leveraged the mobility of oxygen vacancies and external dopant cations to tune catalytic activity in CeO_2 , both as a catalyst and as a host for catalysts (or other active dopants). As explored above, much of cerium oxide's reactivity is derived from the ability to store and

release oxygen (also known as the oxygen storage capacity or OSC)^{57,58} and the ability to tune the accompanying Ce³⁺ sites.^{9,15,59}

1.2.1 *Heterogeneous Catalysis*

The first of two landmark heterogeneous catalysis applications we will discuss in this dissertation is ceria as a support in three-way catalysts (TWCs) for automotive converters. For TWCs, the catalyst requires the ability to simultaneously convert gaseous emissions of hydrocarbons, CO, and NO_x into benign H₂O, CO₂, and N₂, and which typically relies on precious noble metals such as Rh and Pt (**Figure 1.4A**).¹ It was identified early on that the efficiency of a TWC is benchmarked by the OSC of the catalyst and resistance to thermal aging.^{3,5} Pioneering work by Yao and Yao in the early 1980s demonstrated the successful oxidation of CO by ceria, one of the three critical reactions in a TWC, leading to its widespread study and eventual industrial implementation both as a support for noble metals and as a participant in catalysis itself.⁵⁷ Additional studies to optimize ceria demonstrated that the incorporation of dopants such as Zr,^{60,61,62} or additives (Ni, Cu)⁶³ yielded improved OSC by allowing for greater lattice oxygen mobility. The primary conclusion that was elucidated from these studies is that while oxygen storage in CeO₂ may be restricted to the surface, in the presence of dopants or additives there is also participation of bulk oxygen in the storage process.⁶⁰ Furthermore, research demonstrated that ceria played many intertwined roles in the success of TWCs such as promoting noble metal (active catalyst) dispersion, increasing the thermal stability of the Al₂O₃ support, promoting water gas shift and steam reforming reactions, promote CO removal by oxidation of CeO₂ lattice oxygen, and, of course, the storage and release of oxygen.³

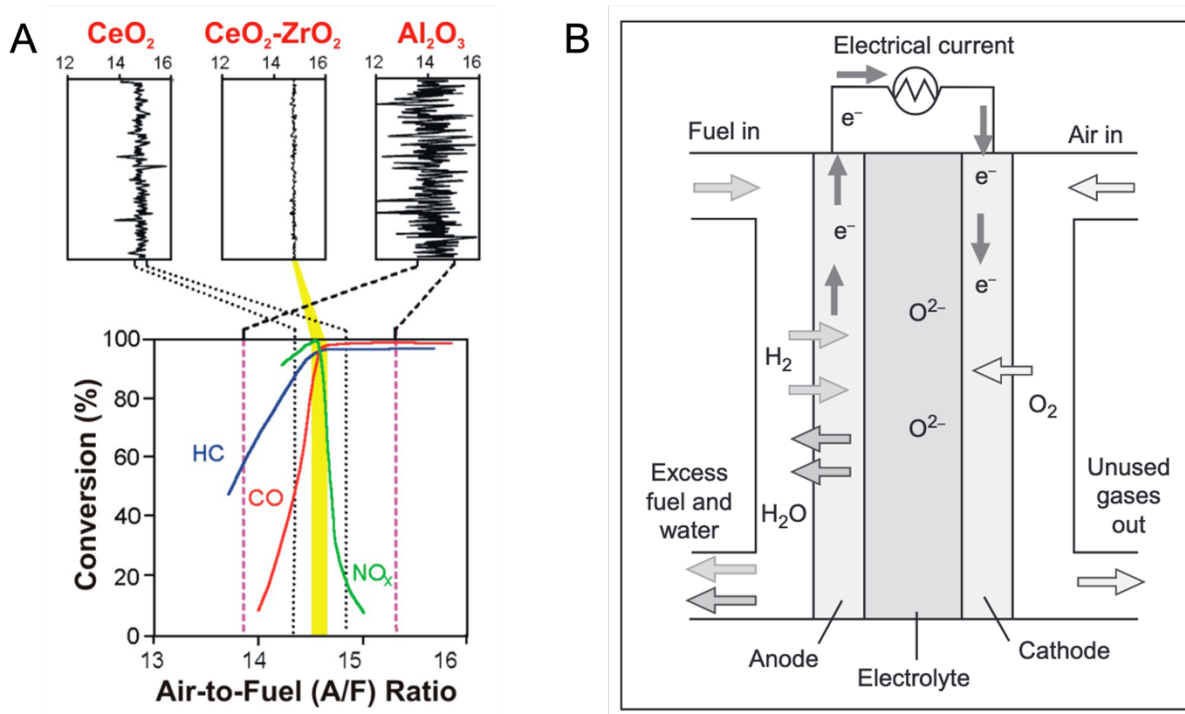


Figure 1.4. (A) Conversion efficiency of hydrocarbons, CO, and NO_x as shown by the Air-to-Fuel ratio with respect to different supports (CeO_2 , $\text{CeO}_2\text{-ZrO}_2$, and Al_2O_3) used in three-way catalysts used with permission from Ref 1. (B) Diagram of a solid oxide fuel cell, emphasizing flow of electrons from cathode through the electrolyte in the form of O^{2-} ions (oxygen ion conductivity) to the anode and external circuit via H_2 dissociation. The solid oxide electrolyte is typically very thin. Figure used with permission from Ref 64.

The other landmark application of ceria is in solid oxide fuel cells (SOFCs), whose design are intended to output electricity, water and heat with H_2 or methane as the fuel source (**Figure 1.4B**).^{1,64} In the early 1960s, several studies showed that La_2O_3 -doped, Y_2O_3 -doped, and Sm_2O_3 -doped CeO_2 could act as an electrolyte and, for some compositions of mixed oxide, as a catalyst in both cathodes or anodes in SOFCs.^{1,21} This is not only because of ceria's ability to shuttle electrons and oxygen atoms, but also the fact that it was potentially compatible with several fuels without suffering from CO poisoning, a common issue in the field. Despite promising beginnings, ceria's performance as an electrolyte yielded mixed results given that the reduction of ceria by the H_2 fuel caused issues with decreasing the open circuit voltage. Interestingly, the

authors showed that if they used a protective layer of yttria-stabilized zirconia (YSZ) on the fuel side of the SOFC, then ceria would cease to reduce and performed better than the YSZ alone.⁶⁵ Since then, several works have investigated the coating of YSZ on CeO₂ electrolytes,^{66,67} doped ceria, and nanostructured ceria for improved electrolyte performance.^{68,69} On the cathode and anode front, it is now well studied and appreciated that the mixed O²⁻ and electron conductivity of ceria is tuned by the doping with lower valent cations (such as Gd³⁺, Sm³⁺, Y³⁺, Ca²⁺, Pr³⁺, and Sc³⁺), where both ionic conductivity and electronic conductivity are needed to produce an efficient SOFC.⁷⁰ For example, the classic example of this is the Gd-doped ceria anode, where authors demonstrated the cell performance increased as a direct result of increased oxygen vacancy concentration due to doping.⁷¹

Finally, we revisit the discussion of solid solutions of CeO₂, which we had discussed on a fundamental structural level with regard to Vegard's rule previously. The maximum amount of dopant tolerated by the fluorite structure is governed mainly by temperature. For oxides with a cationic radius close to the ionic radius of the host lattice, a solubility limit of 15–25% substitution of Ce⁴⁺ is commonly observed at materials prepared around 1000 °C.¹ Beyond these dopant percentages, a miscibility gap is present, yielding an inhomogeneous mixture of CeO₂-rich and dopant oxide-rich phases.

These mixed oxide solutions become relevant to the engineering of TWCs by using nanostructured CeO₂-ZrO₂ (and CeO₂-HfO₂), providing both improved OSC and greater surface area. Despite the ~15% difference in ionic radii between Zr(IV) and Ce(IV), 0.84 Å vs. 0.97 Å, and the difference in structures at room temperature (ZrO₂ is monoclinic, *P*2₁/*c* space group vs. CeO₂ is cubic, *Fm* $\bar{3}$ *m* space group), they are able to form a seemingly homogeneous solid solution. Identification of the many phases based on the relative composition of CeO₂ to ZrO₂ indicates the presence of metastable phases such as tetragonal and hexoctahedral (pyrochlore), between predominantly cubic or monoclinic crystal systems.^{1,18,72,73} Extended X-ray absorption fine structure spectroscopy of the local structure shows that an intermediate compositions such as Ce_{0.5}Zr_{0.5}O₂, the O sublattice is significantly distorted around the Zr atoms instead of the Ce atoms due to longer Zr–O bond lengths, suggesting that these bonds are weaker and the O atoms are more prone to diffusion and contribute to catalysis.^{74,75} Alternative analysis of a Ce_{0.5}Zr_{0.5}O₂ sample by neutron

diffraction revealed the presence of nanodomains of $\text{Ce}_{0.4}\text{Zr}_{0.6}\text{O}_2$ with an average size of 2.5–3.0 nm within a matrix of $\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$, which are not detected by conventional XRD and Raman analyses.⁷⁶

The situation is similar for solid solutions of CeO_2 with 3+ oxidation state lanthanides as an electrolyte in SOFCs.^{1,4} The ionic radius of these elements in the 3+ oxidation state allows for high or complete miscibility with CeO_2 at high temperatures, and their incorporation has been observed to yield oxygen vacancy sites that promote oxygen diffusion and allow hopping of O^{2-} anions from site to site.^{77,78} Curiously, in some cases for these M_2O_3 -doped CeO_2 structures, density and X-ray intensity analysis via an anion vacancy model shows the presence of long-range ordering of the anion vacancies into a C-type rare earth oxide structure that is inferred to promote oxygen diffusion in the materials.^{79,80,81} C-type rare earth oxide structure is characterized by excessive anions in the lattice, leading to a distorted fluorite-type arrangement.⁸²

The conclusion we draw from the discussion of the systems above is that there are still some structural ambiguities in cerium oxide. How do we investigate these more clearly, or is it even possible with our current capabilities? As Montini et al. stated so eloquently in their comprehensive review of CeO_2 -based materials: “After almost 50 years of research, the redox properties of ceria-based materials remain puzzling, and their understanding requires new techniques and knowledge coming from emerging fields of application of these materials...” How do we tie together the multiple different rationalizations of cerium oxide structure (nanodomains, metastable phases, and C-type structures, etc.) to gain a better understanding of its design? While we may not have the answers yet, this dissertation aims to uncover the barest fraction of these mysteries.

1.2.2 Bio-Inspired Catalysis

In the mid to late 2010s, cerium oxide nanoparticles were found to exhibit multi-bioenzyme-mimetic properties, including superoxide dismutase and phosphatase activities.^{9,15,83,84} In 2007, Korsvik and coworkers reported that ceria nanoparticles could act as catalysts that mimic superoxide dismutase (SOD) with a catalytic rate that exceeded that of the enzyme for SOD.⁸³ Around that same time, multiple studies

demonstrated that treatment of mice and rats with nanoceria to address oxidative stress in various cells showed reduced inflammation and cell death, implying that ceria was an apparent antioxidant.^{85,86,87} Korsvik's study pointed towards ceria's radical scavenging abilities as a probable explanation. Because SOD is an enzyme that repairs and reduces damage inflicted by superoxide (the most common free radical in the body), ceria's ability to oscillate between oxidation states differing by one electron ($\text{Ce}^{3+} \rightleftharpoons \text{Ce}^{4+}$) allows ceria to either oxidize $\text{O}_2^{\bullet-}$ by one electron to O_2 or reduce $\text{O}_2^{\bullet-}$ to H_2O_2 (**Figure 1.5A**).^{9,15} By testing different ratios of $\text{Ce}^{3+}/\text{Ce}^{4+}$, they demonstrated that a higher ratio of Ce^{3+} in the CeO_2 nanoparticles exhibited higher SOD-like activity, where a proposed mechanism suggested that the oxygen vacancy sites with adjacent Ce^{3+} ions afforded easy binding and reduction of superoxide to hydrogen peroxide.^{83,59}

This same conclusion was drawn by others when studying another biological reaction of interest: hydrolysis of phosphate ester bonds, which are crucial for regulation of protein activity, synthesis and conversion of energy transfer molecules (ATP, ADP, etc.), and the stability of DNA and RNA.^{88,89} Initially, Tan et al. demonstrated proof-of-concept use of micron-sized cerium oxide particles (1–10 μm) for the dephosphorylation of phosphopeptides, learning that the strong Lewis acidity of Ce^{4+} encouraged coordination of the phosphoryl O atoms to the surfaces of ceria, subsequently making the center phosphorus more electropositive and reactive towards hydroxyls, resulting in a cleaved P–O bond and a liberated phosphate group.⁸⁸ In this regard, the authors equate cerium oxide to a multi-nuclear metal–oxygen complex, akin to that of an enzyme active site wherein synergistic activation effects are at play to yield high catalytic activity. Later, Kuchma et al. reinforced this message with the dephosphorylation of p-nitrophenylphosphate, o-phospho-L-tyrosine, and ATP by 3–5 nm ceria, wherein they concluded that the reactions were actually dependent on the presence of Ce^{3+} sites, and computation pointed towards an $\text{S}_{\text{N}}2$ -type mechanism via inversion of the phosphate group (**Figure 1.5B**).^{89,90} Remarkably, the ceria nanoparticles are inactive towards DNA hydrolysis, although this is tentatively explained by the center phosphorus atom in DNA being too sterically hindered to undergo nucleophilic substitution on the nanoparticle surface. This idea of surface sites on ceria acting akin to an enzymatic site is relevant to the discussions continued in Chapter 2.

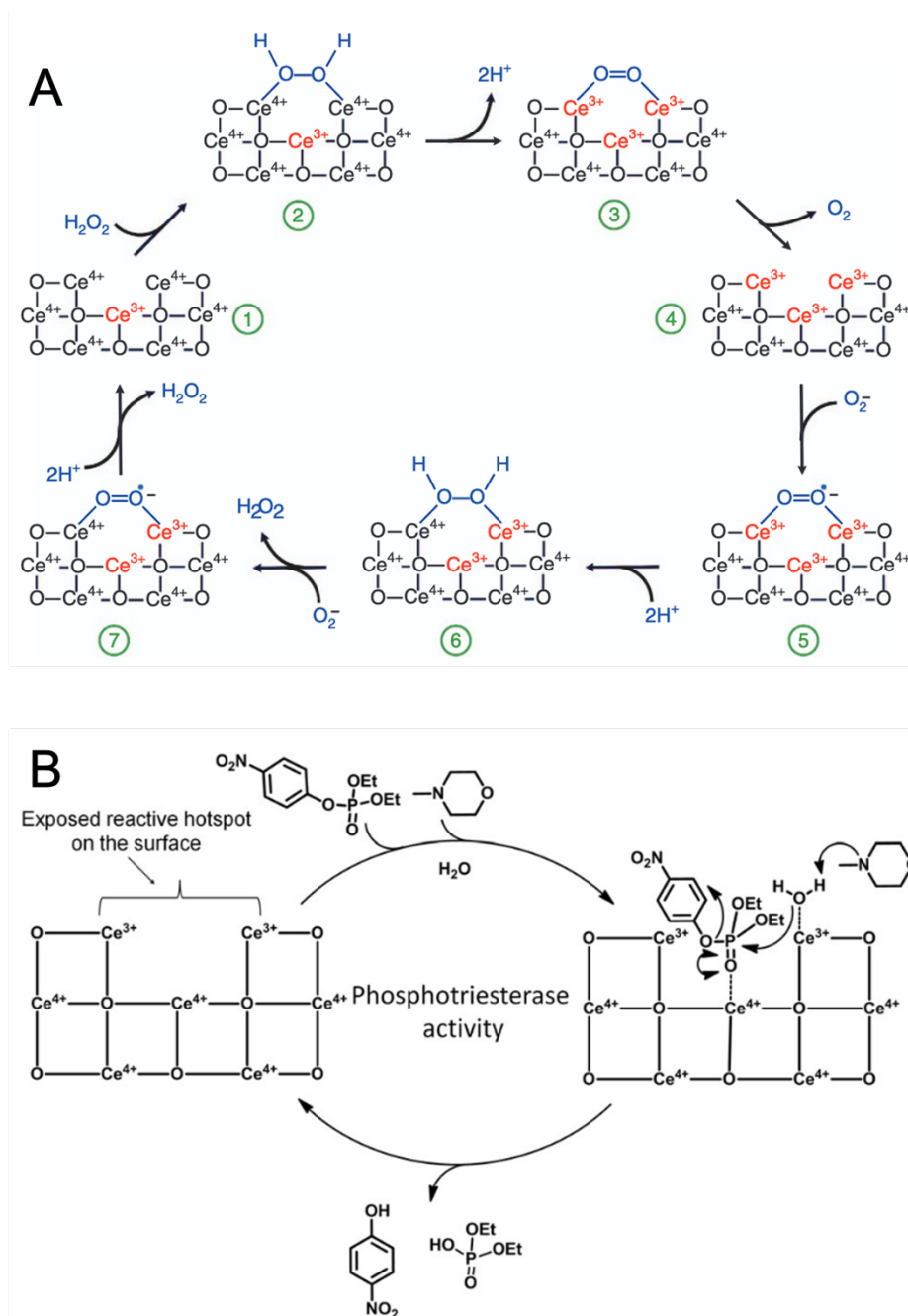


Figure 1.5. (A) Scheme of the proposed reaction mechanism for the dismutation of superoxide by cerium oxide nanoparticles used with permission from Ref 9. (B) Scheme of the proposed reaction mechanism for dephosphorylation of phosphotriesters by cerium oxide nanoparticles used with permission from Ref 90.

1.3 *Emerging Applications: Quantum Information Systems*

Quantum information technology and processing is a mode of information processing based on the principles of quantum mechanics. It relies on quantum systems, such as atoms or molecules, taking on the fundamental pieces of information used in classic computing (bits, which exhibit discrete 0 or 1 values) and becoming quantum bits (qubits) that can represent both 0 and 1 simultaneously.⁹¹ How is this simultaneous 0 and 1 state possible? This phenomenon is called quantum superposition, where the qubit itself is described and measured by probabilities rather than discrete values. These states can be manipulated using a whole host of physical systems, including the electronic states of an atom, the polarized states of a single photon, and the spin states of an atomic nucleus or an unpaired electron. A system that holds multiple qubits can then simultaneously represent many numbers in quantum superpositions, performing many parallel computations, and hence using significantly fewer bits, computational time, and memory than in classic computing.^{91,92} While this concept is not further explored within this dissertation, we must also mention that qubits have the astounding ability to become entangled (which Albert Einstein has described as “spooky action at a distance” in letters to Max Born back in 1947 on the topic of entanglement in quantum mechanics).⁹³ An entangled state is a state shared by two separated qubit particles, regardless of physical distance. Harnessing this entangled state is an area of ongoing research, particularly in the areas of quantum cryptography, quantum teleportation, and quantum dense coding.⁹¹

Realizing the implementation of quantum computing technology and other quantum systems for sensing and communication hinges on one very critical piece: the quantum behavior of these qubits must remain intact during use. The delicacy of this quantum behavior, also referred to as coherence, is not to be underestimated. Before we discuss the loss of coherence, let us discuss what coherence means in simpler terms. An example of quantum technology that might be easier to understand is the laser.⁹² Before the laser, we had light in the form of fire, the lantern, and eventually the lightbulb. These types of light are “incoherent” in that they emit electromagnetic (light) waves continuously but at random with respect to each other. In the case of a laser, quantum-mechanical effects of the light source allow it to produce light waves that are

in phase with each other, creating a coherent light source that is useful for a plethora of applications, distinct from lightbulbs.⁹²

Achieving coherence of quantum bits allows us to reach beyond the limitations of classical computing in the same fashion. And to return to the delicacy of coherence, any perturbations from the environment (temperature,* magnetic fields, electric fields, radiation, defects within the system, sometimes other qubits, etc.) can cause loss of phase information in quantum systems, also called decoherence.⁹⁴ Decoherence comes in several forms: by measuring an ensemble of qubits, there may be interference of the environment, which will cause quantum behavior to decay as previously stated, but also the act of measurement of the ensemble can create interference where qubit-to-qubit or repeat trial-to-trial variance in the oscillations leads to a natural decay of quantum behavior over time. These decoherence parameters, which are often measured by electron paramagnetic (EPR) spectroscopy, are identified by time scale factors: T_1 is the timescale of decay of the qubit energy (I think of it as how long the qubit is “on”) which is decayed by environmental effects, and T_2 is the timescale of decay of the qubit coherence (I think of it as how long the qubit is “in phase” or in a superposition state). The measurements of these time scales via EPR and their processes can be visualized by considering spin magnetization vectors projected onto a complex unit sphere called the Bloch sphere as seen in **Figure 1.6**.⁹⁵ The complication of an ensemble measurement and related qubit-to-qubit or trial-to-trial variance is identified by one final timescale: T_2^* .^{92,94} It has been established that the coherence (in-phase behavior, T_2) lifetime of the qubit is inherently limited by the energy lifetime (T_1) of the qubit, by the rule $2T_1 \geq T_2$ and that in most systems $T_1 \gg T_2$. While both are necessary for qubit operation, the longer T_2 is, the better it is for quantum computation.⁹²

* The use of dilution refrigerator, a cryogenic device that allows for the cooling of systems down to 0.002 Kelvin, is common (if not required) for the implementation of many quantum systems.

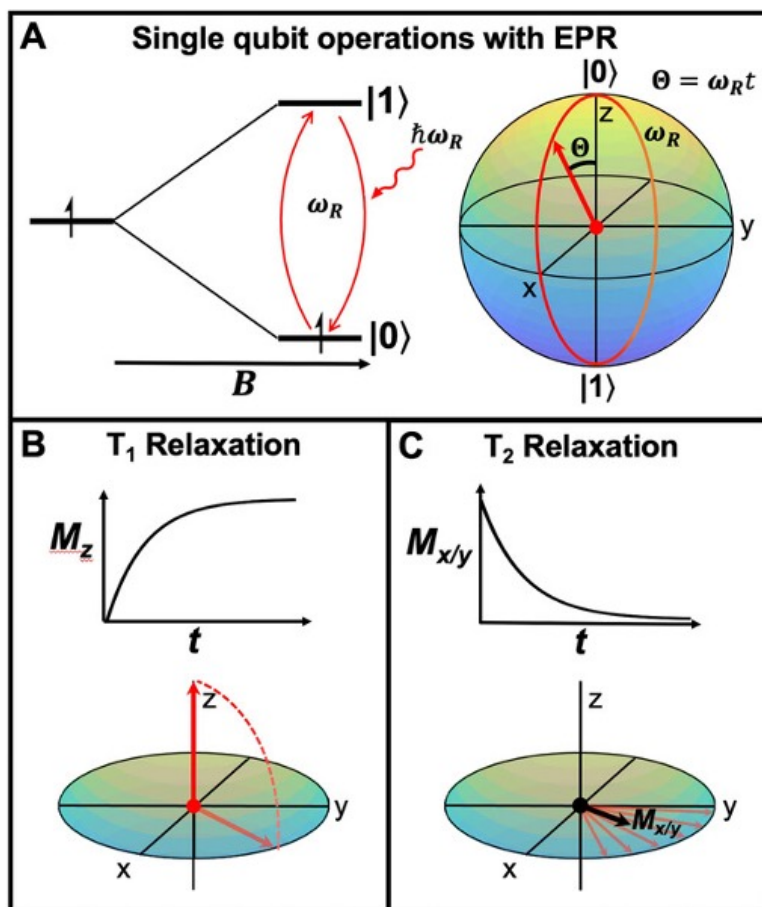


Figure 1.6. Principles of qubit measurements in EPR spectroscopy. (A) Magnetically split electron spin sublevels serve as the qubit platform. The quantum state can be controlled by the microwave pulse length t , which alters the wave function parameter Θ in the Bloch sphere representation of a single qubit. (B) T_1 relaxation, depicted as the recovery of net longitudinal magnetization M_z in the rotating frame representation. (C) T_2 relaxation, depicted by the decrease in the net transverse magnetization vector $M_{x/y}$ (black arrow) as the ensemble of spins (red arrows) lose their phase coherence. The T_1 contribution to T_2 is not shown. Figure used with permission from Ref 95.

Perhaps you're wondering what a qubit actually looks like in reality and in research. While we will not discuss the full extent of qubit research in this introduction, qubits have been developed and studied in a wide range of systems, given their requirements of needing a quantum system that exhibits a 0 and 1 state. Examples in research include: zero-resistance currents in superconductors, nuclear spins in molecules,

energy levels in trapped atoms or ions, polarization states of photons, and finally the method in which we are interested in investigating: optically active spin dopants in solid-state materials.^{92,96}

1.3.1 *Solid State Spin Defects*

One leading qubit candidate is the diamond nitrogen–vacancy (NV^{-1}) center: it is an optically addressable quantum system that may be initialized, manipulated, and measured with high fidelity at room temperature (!!!).^{96,97,98} Why is this such a successful qubit? This is primarily due to the fact that the nitrogen–vacancy center, comprised of a carbon vacancy and an adjacent substitutional negatively charged nitrogen impurity, within the diamond lattice, comprised of covalent tetrahedral carbon bonds with a wide bandgap, is a highly localized electronic bound state with respect to the host lattice.⁹⁶ This localization within the lattice shields the unpaired spin qubit (up or down for 0 or 1) exceptionally well from sources of decoherence within the lattice, yielding coherence times (T_2) of up to 1.8 ms at room temperature.⁹⁹ The main source of decoherence in a strongly isolated system, like the NV^{-1} center, is the nuclear spin bath (strongly coupled nuclear spins from proximal ^{13}C atoms) can cause dephasing. For samples with natural isotope abundance, containing some non-zero fraction of nuclei with unpaired nuclear spins, they can strongly couple with the electron spin from the NV^{-1} center as far away as 1 nm (10 angstroms).⁹⁸

To reproduce the qualities of the NV^{-1} center in other qubit candidates, there are several requirements the spin defect center and its host must meet:⁹⁶

1. Qubit must have a bound state that is paramagnetic and long-lived. It must also have an energy splitting between two of the state’s spin sublevels. In the case of qubit manipulation by electron spin resonance (EPR), the size of this energy splitting must fall within the radio frequency spectrum.
2. Qubit must be able to be optically pumped. This involved an optical transition from a ground state to an excited state, followed by a spin-selective decay path.
3. Qubit must have luminescence that varies by sublevels in some differentiable way. The fluorescent transition from an excited state should be spin-conserving for probing the qubit.

4. Optical transitions used to prepare and measure the qubit states must be lower in energy than the energy required to transfer an electron into or out of the defect center from the electronic states of the host (they must not interfere with the electronic transitions of the host material).
5. Bound states are separated from each other by energies large enough to avoid thermal excitation between them. Two bound states cannot be too close in energy or thermal excitations may couple states and decohere.
6. The host lattice must have a wide bandgap to accommodate a deep center so as to comply with requirement 4 listed above.
7. The host lattice must have small spin-orbit coupling to avoid unwanted spin flips in the defect-bound states.
8. The host lattice must be available as high-quality, bulk or thin-film single crystals to avoid imperfections or paramagnetic impurities that interfere with the defect spin state.
9. Constituent elements of the host lattice must have naturally occurring isotopes of zero nuclear spin so that spin bath effects may be mitigated.

To this end, rare earth ions in solid-state crystals have been identified as possible spin defect centers due to the shielding provided by their filled outer electronic shells and $4f$ electrons with narrow and stable optical and spin levels.^{98,100,101} For example, research has shown that rare earth ions such as Er^{3+} offer long spin coherence and narrow, stable optical transitions.^{101,102,103}

1.3.2 *Cerium Oxide as a Spin Qubit Host*

In 2020 and 2022, two computational studies evaluating the suitability of host materials suggested that cerium oxide was a promising host for quantum defects due to its high natural abundance of spin-free isotopes.^{104,105} Specifically, Kanai et al. used cluster correlation expansion (CCE) computational techniques to simulate the coherence times (T_2) of an electron spin interacting with a large number of nuclear spins by dividing the spins into small subsets of interacting spin clusters.¹⁰⁵ CCE calculations allowed the authors to examine a large pool of candidate materials (over 12,000 host materials of binary, ternary, and quaternary

composition) and predict T_2 times limited only by interactions of the nuclear spin bath (of course, others exist, but this assumes no other paramagnetic or lattice defects), suggesting a fundamental limit for spin decoherence. Of 27 materials identified as having coherence times longer than 10 ms, CeO_2 was identified as having the longest calculated coherence time, a whopping 47 ms! Other materials from these simulations were oxides and sulfides of Fe, Ca, and Ni as cations.¹⁰⁵

Over the course of my Ph.D., two seminal works have already been published that probe the use of CeO_2 as a host for Er^{3+} as a spin qubit system.^{106,107} The first by Grant et al., where they investigated the optical and microstructural characterization of Er^{3+} doped in epitaxially layered cerium oxide on silicon substrates. Here, they're forming what is akin to bulk bulks with Er^{3+} concentrations near 2–3 ppm. They showed by optical characterization and EPR that the Er^{3+} signal is exceptionally long-lived (optical excited state lifetime $T_1 \sim 3.5$ ms at 2 ppm Er) and broadens as concentration is increased from 2–3 ppm up to 130 ppm.¹⁰⁶ The second by Wong et al. established the benchmarks for Er^{3+} -doped CeO_2 in nanocrystalline materials, and calculated their dopant percentages down to less than one Er^{3+} atom per nanocrystal, with corresponding $T_2 \sim 776$ ns.¹⁰⁷ The limitations of these studies were discussed, predominantly that the surfaces of CeO_2 nanocrystals are very prone to Ce^{3+} defect formation and vacancies, and because the nanocrystal sizes were only 7 nm, that even the hydrogen spin bath from the ligands and solvent surrounding the nanocrystals had a small impact on the dephasing.

Follow up studies published in 2025 looked again at epitaxial single-crystals (CeO_2 film, doped with 2–3 ppm Er^{3+}) grown on silicon where they achieved observed T_2 times in the microseconds region.^{108,109} They also identify Ce^{3+} defects as a contributor to their signal dephasing.¹⁰⁹ But, it is an encouraging result nonetheless that Er^{3+} doped CeO_2 platforms could be feasibly used for quantum computing with continued investigation.

1.4 Cerium Oxide Nanocrystal Synthesis Strategies

Cerium oxide nanocrystals can be synthesized in a multitude of different ways: hydrothermal, solvothermal, aqueous precipitation, reverse micelle, thermal decomposition, and flame spray methods have all been reported.⁹ Additionally, the nanocrystals can be synthesized bare or with a coating, such as a polar/nonpolar ligand that binds or adsorbs to the surface of the nanocrystal or a hydrophobic/hydrophilic polymer that engulfs the nanocrystals, thereby imparting solubility to the nanocrystal. These various synthetic methods are all determinants of nanocrystal size, morphology, surface condition, structural arrangement, and solubility.⁹

Despite the tunability of CeO₂ by a myriad of different syntheses, cerium oxide synthesis and, more specifically, controlling its nucleation, growth, and defect structure is still very challenging. The two simplest approaches for CeO₂ nanocrystals are by coprecipitation, where alkaline solutions (NaOH, ammonia, etc.) are combined with cerium salts as precipitating agents, and by hydrothermal synthesis, typically involving water as a solvent at elevated temperatures and pressures.^{1,110} Within these syntheses, the most commonly used experimental variables that determine nanocrystal characteristics are the following: cerium concentration, precipitating agent concentration, reaction temperature (typically ≥ 150 °C), and reaction time. A comprehensive summary of the resultant morphologies from changing experimental variables is summarized by Xu et al.¹¹⁰ Hydrothermal syntheses may also use ligands or surfactants to mitigate the quick precipitation of small spherical crystals (the typical product from a standard coprecipitation synthesis) and control their dimensions and shape with greater fidelity, for example, using oleic acid or oleate anions to form nanocubes.^{111,112} It has been shown that the shape-selective growth of CeO₂ nanorods vs. nanocubes can also be tuned by the cerium salt precursor anion using Cl⁻ vs. NO₃⁻ due to the fact that the nitrate anion has a significant influence on the dissolution–recrystallization process occurring in hydrothermal reactions.¹¹³ Another study suggests that the hydroxide concentration (precipitating agent) and temperature were driving the control between nanorods and nanocubes due to a dissolution–recrystallization mechanism.¹¹⁴ While these are not in direct contradiction to each other, it

highlights a need for a delicate balance between each component of the synthesis when targeting the desired product. After attempts to reproduce many syntheses described above, my observation is that the most reliable syntheses that produced homogeneous products were often those with a ligand (also described as a capping agent) to control morphology and growth consistently, although they typically yielded a very small size range (5–7 nm particles). On the other hand, morphologies observed in hydrothermal and co-precipitation syntheses without capping agents were often mixed but spanned a much larger size range (5–50 nm, with greater polydispersity).

One final synthesis we will discuss here is the high-temperature thermal decomposition of cerium precursors in organic solvents with organic ligands, such as oleylamine, to form nanocrystals. In these reactions, water and air are avoided to have finer control over the introduction of the oxygen atom sources and have been adapted from syntheses of other metal oxide nanocrystals, such as iron oxides and manganese oxides.¹¹⁵ By toggling parameters in the synthesis, such as organic ligand identity, cerium precursor, and additives (such as including distilled water back into the synthesis), they showed nanocrystal size and monodispersity were able to be controlled within a range (approximately 2–10 nm). Unlike the co-precipitation and hydrothermal methods, the synthetic handles are able to be more finely tuned, however, as mentioned previously, the size control is still limited to under 10 nm.

1.5 Motivating The Dissertation Herein

Thus far, we have discussed the nature of cerium oxide nanocrystals, both in the many ways they have been studied and manipulated for various applications. The question that arises now: where does that leave this dissertation? There is certainly a considerable body of literature investigating CeO₂. This dissertation aims to investigate two facets. In Chapter 2, we intentionally defect-engineer CeO₂ and then examine its surface active sites for organophosphate hydrolysis, which has implications for better understanding ceria's use as a heterogeneous catalyst for biological and bio-inspired applications. Ultimately, we ask whether we can address the structural complexity of these nanocrystals. In Chapter 3, we take the lessons learned from

intentional defect engineering of the nanocrystal to ask whether we can transform defect-riddled cerium oxide into a suitable host lattice for lanthanide-based electron spin qubits. We ask whether we can establish robust, benchmark values for ceria's capabilities as a nanocrystal host for a system other than erbium. This dissertation would perhaps not exist if the answer were no, but I hope these questions compel you to read further.

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Chapter 2.

CeO₂ Nanoparticle Doping as a Probe of Active Site Speciation in the Catalytic Hydrolysis of Organophosphates

This chapter is adapted with permission of the American Chemical Society from “CeO₂ Nanoparticle Doping as a Probe of Active Site Speciation in the Catalytic Hydrolysis of Organophosphates,” Emily Miura-Stempel., Ashley G. Oregon, Samantha M. Harvey, James. J. De Yoreo, Chun-Long Chen, and Brandi M. Cossairt, *ACS Applied Nano Materials*, **2024**, 7 (13), 15498–15507. Copyright 2024 American Chemical Society.

2.1 Introduction

Organophosphate degradation, also known as dephosphorylation, involves cleaving P–O bonds to eliminate phosphate groups. This process holds significance in various chemical contexts, from the degradation of environmentally harmful phosphorylated compounds such as nerve agents and pesticides to the critical processes within proteins.^{1,2,3,4} The removal of phosphate groups is also pertinent for extracting and recycling phosphorus from phosphorylated molecules, such as phospholipids and nucleic acids, for fertilizer production.⁵ In nature, phosphotriesterases catalyze this reaction at a dinuclear metal site with a bridging hydroxide, where substrate hydrolysis proceeds via a direct nucleophilic attack by the bridging hydroxide.^{6,7,8,9,10} Efforts to influence organophosphate reactivity have led to the rational redesign of the organophosphate binding pocket, akin to manipulating an active site ensemble at a molecular or heterogeneous surface.⁸ Furthermore, the structural motif of a dinuclear metal site with a bridging hydroxide at the active sites of these enzymes has inspired synthetic models, including dinuclear zinc complexes,^{11,12,13} zirconium metal-organic frameworks,^{14,15} and metal oxide nanomaterials.^{16,17,18}

Bulk and nanocrystalline CeO₂ (ceria) are particularly interesting for organophosphate catalysis. There is a multitude of studies investigating CeO₂ nanomaterials for a wide range of biological,^{19,20} biomedical,^{21,22,23} and heterogeneous catalysis applications,^{24,25,26} all originating from the redox properties of ceria, specifically the mild potential required for the reduction of Ce⁴⁺ to Ce³⁺ and the associated oxygen vacancy defects that are formed to compensate charge.^{27,28,29} For dephosphorylation, it is generally agreed that a mixture of Ce³⁺ and Ce⁴⁺ is essential for high catalytic activity.^{5,30,31,32,18} A landmark study was published by Kuchma et al. where they showed that the cleavage of phosphate ester bonds in *para*-nitrophenol phosphate, ATP, and *o*-phospho-L-tyrosine all rely on the presence of Ce³⁺ sites for activity. Subsequent studies have agreed with this observation, notably the work by Vernekar et al., where they demonstrated that ceria could be vacancy-engineered to produce Ce³⁺ on the nanoceria surface.¹⁸ Additionally, several studies have argued that certain ceria facets have better reactivity not just for their stoichiometry but due to differences in –OH and substrate adsorption ability,^{33,34,32} concentration of oxygen vacancies,⁶ and Lewis acidity.³ For example, Tan et al. determined that the facet-dependent reactivity is derived from the higher Lewis acidity of Ce⁴⁺ compared to Ce³⁺, suggesting that a critical feature in the activation of hydrolysis requires a balance of Ce⁴⁺ to Ce³⁺ sites.³

A common strategy to control CeO₂ defects is using trivalent M³⁺ dopants to tune the relative concentrations of Ce³⁺ and oxygen vacancies, which are intrinsically related. This is because doping with an aliovalent metal can result in the loss of O²⁻ ions in the lattice and Ce⁴⁺ reduction to Ce³⁺ for charge compensation. Several studies have leveraged dopants to tune catalytic activity in CeO₂ for a range of small molecule activation and degradation reactions.^{35,36,37,38,39,27,40} However, the literature prompts a debate on whether a direct relationship exists between oxygen vacancy concentration and catalyst performance. Some have found a strong relationship between dopant-controlled oxygen vacancy concentration and catalytic activity. For example, work by Wang et al. suggested there is a linear relationship between oxygen vacancy concentration and catalytic activity in the Prins condensation–hydrolysis reaction catalyzed by Pr-doped CeO₂.^{41,42,5} In contrast, Basina et al. demonstrated that the best catalytic activity was not necessarily correlated with the highest oxygen vacancy concentration in a study of CO oxidation at M-doped CeO₂

catalysts (M = Sm, Co, Cu, and Cu/Co).⁴³ A related study of the role of oxygen vacancies in Y-doped CeO₂ for CO oxidation suggested that lightly doped CeO₂ and related oxygen vacancies improved catalytic activity, but increasing oxygen vacancies further resulted in observing ordering of oxygen vacancy microdomains that drastically decreased activity.⁴⁴ In the case of organophosphate degradation, the importance of Ce³⁺, oxygen vacancies, dopant identity, dopant concentration, and their interplay has yet to be determined.

In this work, we investigated using trivalent dopants, including Y³⁺, Cr³⁺, In³⁺, and Gd³⁺, for CeO₂ catalyst design and probed the active site speciation to further our understanding of oxygen vacancies in catalytic degradation of organophosphates. We chose dopants that spanned a wide range of ionic radii and Lewis acidity values to tune the dephosphorylation activity of dimethyl-*p*-nitrophenol phosphate (DMNP), a model organophosphate compound often used as a nerve agent simulant whose hydrolysis can be monitored using UV–visible adsorption spectroscopy. The doped nanoparticles were characterized by powder X-ray diffraction (PXRD), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy, showing the impacts of each dopant on the nanocrystal surface in terms of dopant concentration, lattice distortion, oxygen vacancy concentration, and Ce³⁺ concentration. This detailed structural characterization has allowed us to correlate dephosphorylation activity across the series, revealing the critical role of generating specific active site ensembles at controlled concentrations to positively impact catalytic outcomes. Similar to prior observations of CeO₂ reactivity,^{43,44} we have found that there are a combination of synergistic effects that positively impact catalysis, such as the Ce³⁺/Ce⁴⁺ ratio, oxygen vacancies, lattice strain, and relative proximities of Ce⁴⁺ to oxygen vacancies and Ce³⁺ to generate an active site ensemble for efficient catalysis.

2.2 Results and Discussion

2.2.1 Structural Characterization of CeO_2 and $M\text{-CeO}_2$

The undoped and doped CeO_2 samples were synthesized via a biphasic hydrothermal method adapted from Yang and Gao,⁴⁵ resulting in monodisperse, colloiddally stable, oleic acid-capped nanocrystals, as depicted in the transmission electron microscopy (TEM) images in **Figure 2.1A-E**. High-resolution TEM (HRTEM) images in **Figure 2.1F** revealed highly crystalline lattice fringes of CeO_2 assigned as the (111) facet, with a measured lattice spacing of 0.31 nm (**Figure 2.2**). The nanoparticles were annealed at 500 °C to remove the oleic acid ligands, as seen by the change in thermogravimetric analysis (TGA) profiles, yielding a flaky black powder used directly for catalysis (**Figure 2.3**). The powder X-ray diffraction pattern (PXRD) of all samples matched the reported fluorite CeO_2 XRD profile (**Figure 2.1G**).

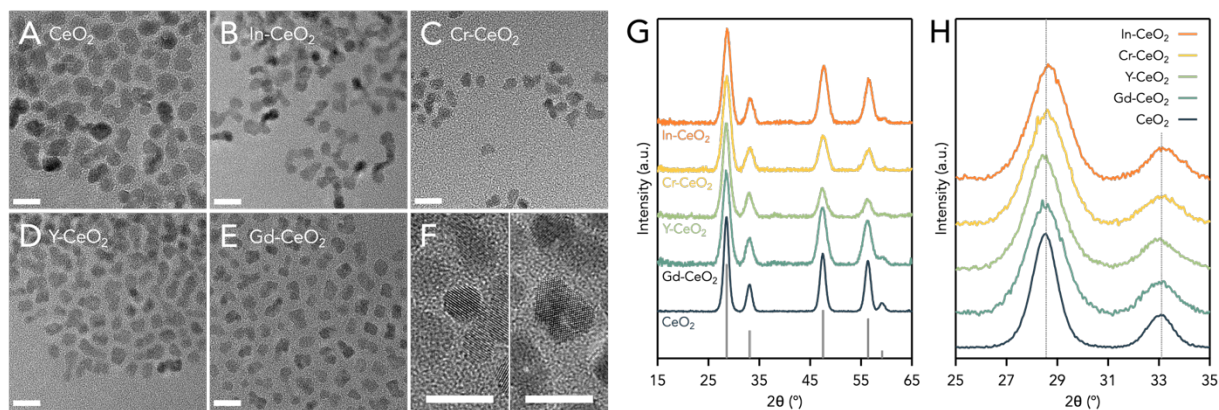


Figure 2.1. (A-E) TEM images, (F) HR-TEM images of undoped CeO_2 , and (G-H) PXRD of doped and undoped CeO_2 , with reference to ICSD 72155.⁴⁶ (All scale bars are 10 nm.)

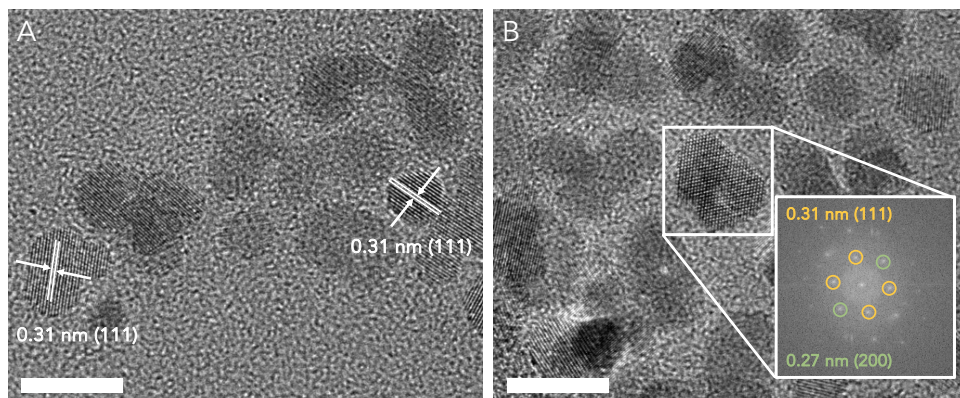


Figure 2.2. High resolution TEM of undoped as-synthesized CeO₂ showing (A) lattice fringes measured to be (111) plane, and (B) fast Fourier transform pattern showing both (111) and (200) planes. All scale bars are 10 nm.

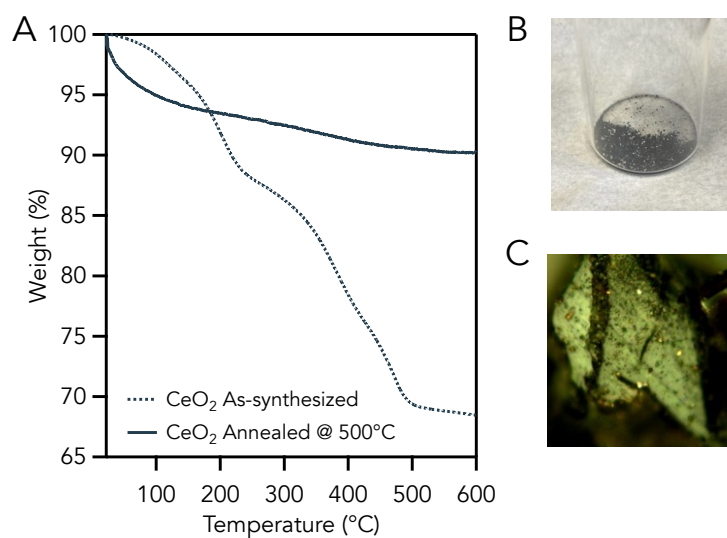


Figure 2.3. (A) TGA profile of as-synthesized and annealed CeO₂, (B) photo of annealed CeO₂ nanoparticles as a flaky black powder, and (C) 50x magnified image of a CeO₂ flake.

The peaks were fitted with Pseudo-Voigt line shapes, providing good approximations of nanoparticle diameter, strain, and lattice constant, as summarized in **Table 2.1** (see **Figure 2.4** for Pseudo-Voigt fittings and residual curves).⁴⁷ Using the Scherrer equation, the average nanoparticle diameters were calculated to be 6.9 ± 0.2 nm, 5.0 ± 0.4 nm, 4.8 ± 0.3 nm, 5.2 ± 0.3 nm, and 4.8 ± 0.5 nm for CeO₂, In-CeO₂, Cr-CeO₂,

Y-CeO₂, and Gd-CeO₂ respectively. Comparison with TEM images suggested minimal changes in nanoparticle size post-annealing (**Figure 2.5**). Consistent PXRD between as-synthesized and annealed samples further supported this observation (**Figure 2.6**).

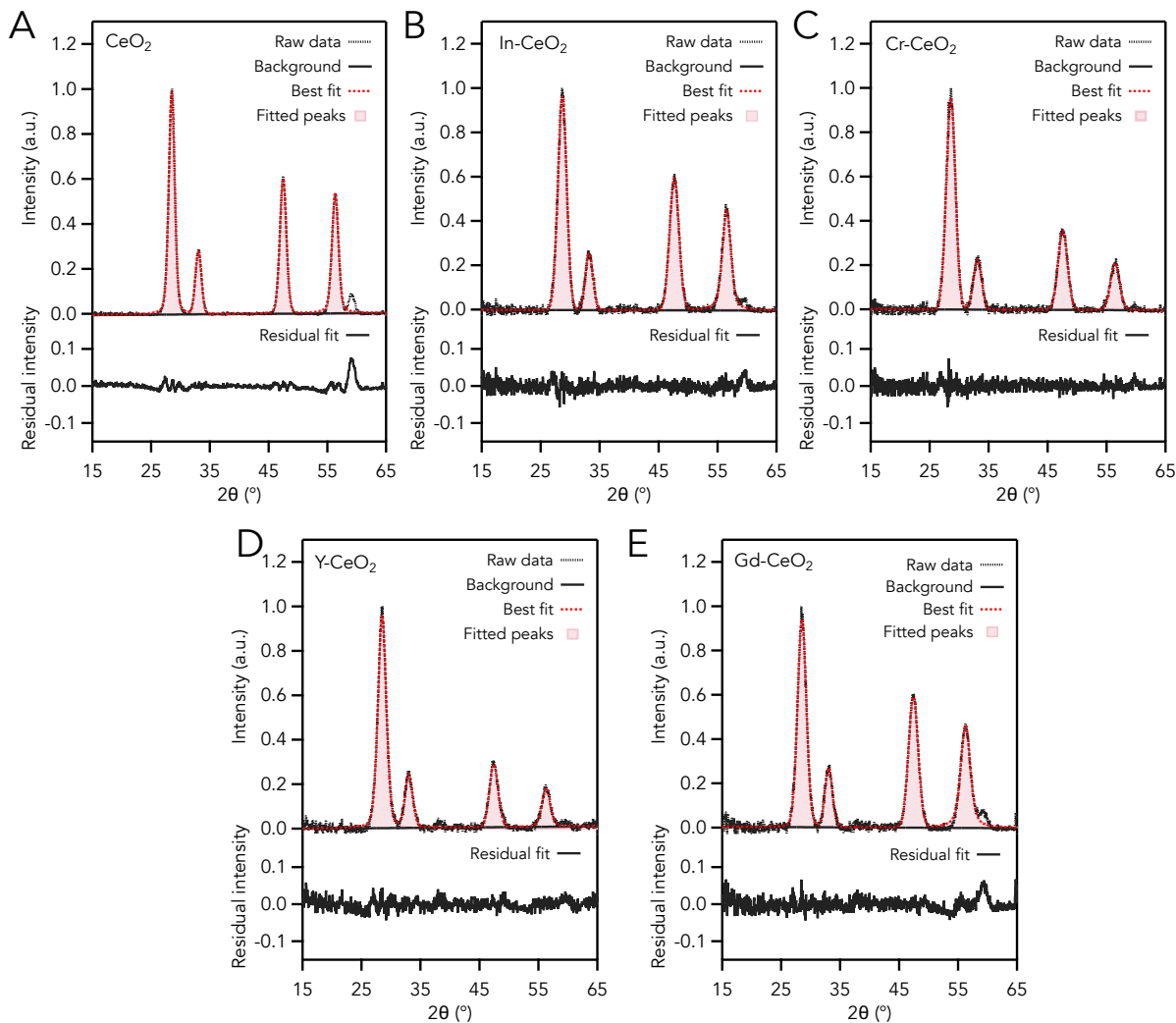


Figure 2.4. Multiplexed Pseudo-Voigt fits and residual fits for PXRD data of (A) undoped CeO₂, (B) In-CeO₂, (C) Cr-CeO₂, (D) Y-CeO₂, and (E) Gd-CeO₂. By Scherrer analysis, all doped CeO₂ diffractograms displayed shifts to smaller size domains by ~1.9 nm on average compared to undoped CeO₂. This decrease in particle size has been reported in previous studies of CeO₂ doping where dopants such as Cu, Co, and Gd all produce a smaller mean diameter compared to undoped CeO₂.^{43,48}

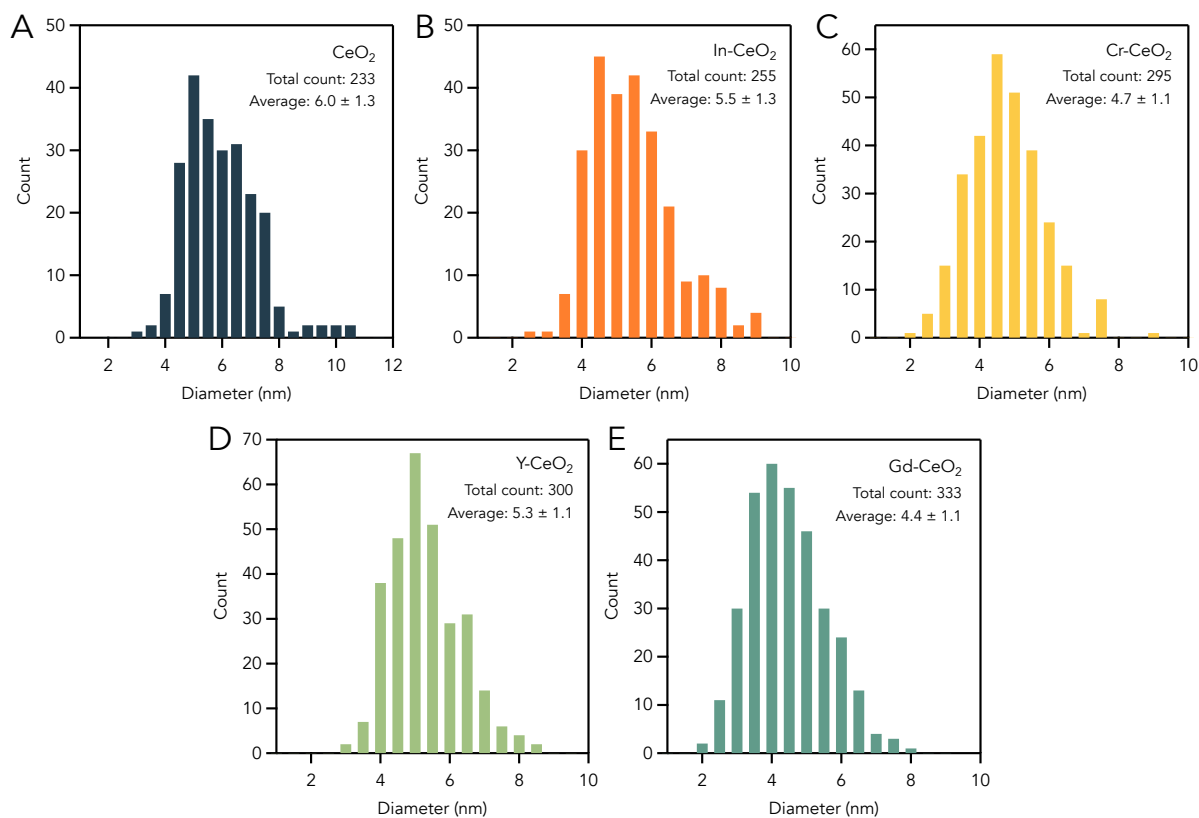


Figure 2.5. TEM diameter sizing distributions for (A) CeO₂, (B) In-CeO₂, (C) Cr-CeO₂, (D) Y-CeO₂, and (E) Gd-CeO₂.

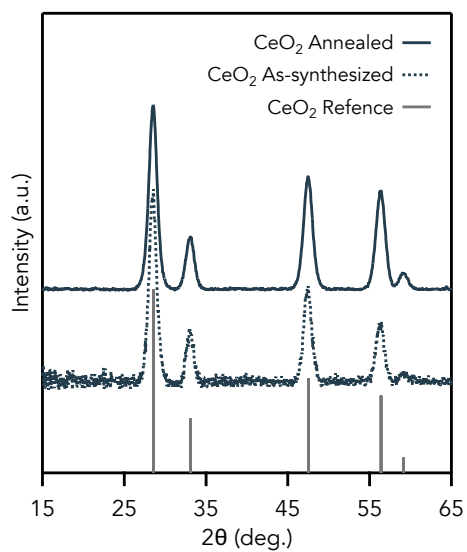


Figure 2.6. PXRD of CeO₂ after annealed at 500°C and as-synthesized CeO₂.

We observed subtle 2θ shifts indicative of doping in the PXRD patterns. The peaks shift to lower 2θ for Y-CeO₂ and Gd-CeO₂, correlating to an expansion of the lattice as expected for Y³⁺ and Gd³⁺ dopants, which have ionic radii slightly larger than Ce⁴⁺ (1.019 Å, 1.053 Å, and 0.97 Å for Y³⁺, Gd³⁺, and Ce⁴⁺ respectively).⁴⁹ The subtle changes in lattice constant also reflect this expansion for CeO₂, Y-CeO₂, and Gd-CeO₂, as listed in **Table 2.1**. The dopant effect is relatively muted because the ionic radii of Y³⁺ and Gd³⁺ fall within the ionic radii of Ce⁴⁺ (0.97 Å) and Ce³⁺ (1.143 Å). Conversely, for Cr-CeO₂ and In-CeO₂, peaks shifted to higher 2θ , indicating lattice contraction due to their smaller ionic radii (0.615 Å for Cr³⁺ and 0.92 Å for In³⁺).⁴⁹ The lattice constants show a corresponding contraction.

Table 2.1. Summary of XRD analysis. ^aICP-OES

Sample	Scherrer Diameter (nm)	W-H Diameter (nm)	W-H Strain (ϵ , $\times 10^{-3}$)	Lattice Constant (Å)	M ³⁺ dopant (%) ^a
CeO ₂	6.9 ± 0.2	6.8 ± 0.4	−0.2	5.415(3)	—
In-CeO ₂	5.0 ± 0.4	4.9 ± 0.9	−0.5	5.393(1)	9.5
Cr-CeO ₂	4.8 ± 0.3	4.5 ± 0.6	−1.2	5.405(2)	11.8
Y-CeO ₂	5.2 ± 0.3	4.9 ± 0.6	−0.8	5.419(4)	15.0
Gd-CeO ₂	4.8 ± 0.5	5.5 ± 1.3	2.7	5.418(1)	15.8

In addition to Scherrer analysis, we applied the Williamson-Hall (W-H) equation to estimate nanoparticle diameters and strain values (**Figure 2.7**).^{50,51} As shown in **Table 1**, the diameters calculated by the W-H equation are in close agreement with those calculated by the Scherrer equation. Undoped CeO₂ exhibits the lowest relative strain, with a negative slope indicating slight lattice contraction. We observed a small trend for In-CeO₂ (9.5% In³⁺) and Cr-CeO₂ (11.8% Cr³⁺), corresponding to more negative strain values for lattice contraction as expected of smaller ionic radius dopants. On the other hand, Gd-CeO₂ shows lattice expansion, resulting in a positive strain value due to the larger ionic radius of Gd³⁺. Curiously, Y-CeO₂

displays a negative strain value that we attribute to the unique surface of Y-CeO₂ caused by local oxygen vacancy microdomains as characterized by Yang et al.⁴⁴

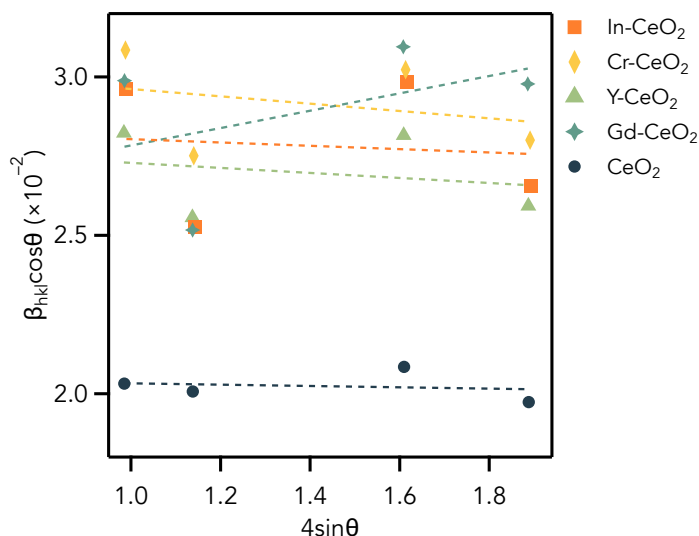


Figure 2.7. Williamson-Hall equation linear fits for all samples.

The total dopant percentages were confirmed by Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP-OES), revealing differing dopant incorporation despite adding an equivalent mol % of dopant metal salt to each reaction (15 mol % with respect to Ce). Variations in precursor reactivity, diffusion, and solubility of the metal in the lattice contribute to this non-uniformity.^{52,38,39} Notably, the Y³⁺ and Gd³⁺ dopants exhibit equal incorporation at the intended dopant mol %, likely due to the similarity in ionic radius to Ce⁴⁺. Interestingly, In³⁺ and Cr³⁺ show similar under-incorporation, possibly due to lower Lewis acidity and oxophilicity.^{53,54} With these findings, we confirmed successful dopant incorporation and preservation of nanoparticle size and crystallinity post-annealing.

2.2.2 Characterizing CeO₂ Surface Defects

To characterize the defects introduced by the M³⁺ dopants, we performed X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. XPS allowed us to measure the surface composition of the nanoparticles, including relative elemental ratios and the ratios of Ce³⁺ and Ce⁴⁺ from the Ce 3d spectra, as

shown in **Figure 2.8A** and summarized in **Table 2.2**. As opposed to ICP-OES, which provides the total atomic composition of the samples, XPS provides insight into non-uniform incorporation by preferentially probing the surface/near surface elemental composition. Consistent with previous studies, the observed discrepancies between XPS and ICP-OES measurements reflect a higher presence of dopant at the surface.^{52,38,39} Notably, the Y^{3+} was measured to be 15.0% by ICP but 28.5% by XPS, suggesting that the Y^{3+} is concentrated on the surface and that the diffusion into the lattice was lower for this sample. Similarly, Cr^{3+} showed higher surface concentration (11.8% by ICP versus 17.5% by XPS), whereas In^{3+} and Gd^{3+} appear more homogeneously distributed throughout the lattice.

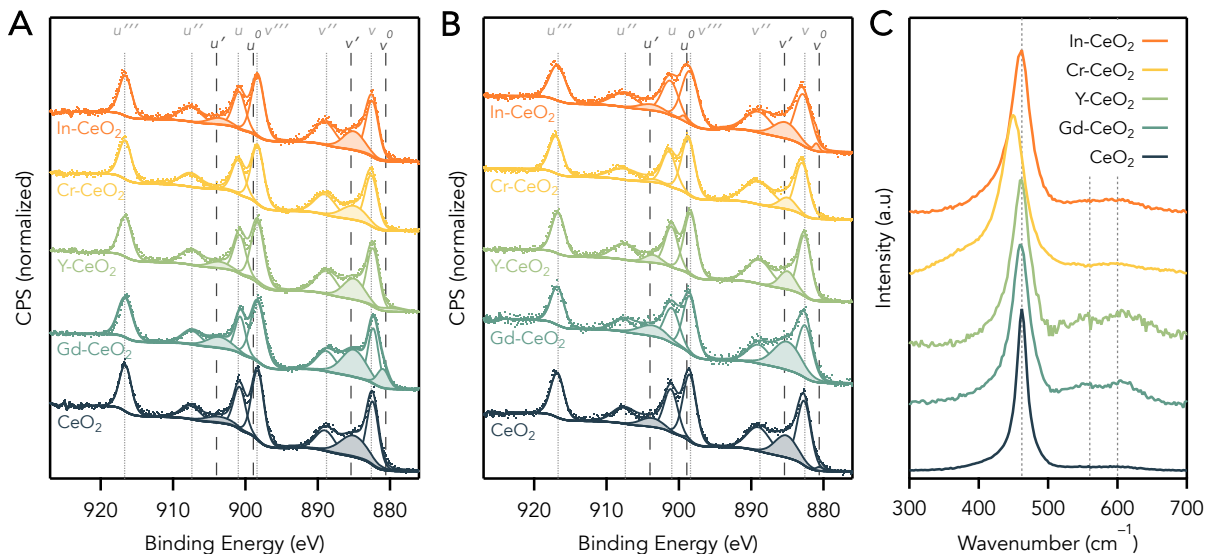


Figure 2.8. High-resolution Ce 3d XPS spectra of (A) as-synthesized samples and (B) after annealing followed by dispersion in pH 10 water. (C) Raman spectra ($\lambda_{\text{ex}} = 514 \text{ nm}$) of samples featuring the characteristic F_{2g} mode for CeO₂.

We determined the percentages of Ce^{3+} from the total measured Ce^{3+} and Ce^{4+} to quantify the impact of the presence of the M^{3+} dopant on inducing further speciation in the CeO₂ lattice in both the as-synthesized samples with native oleic acid ligands and the samples after annealing and dispersion in pH 10 water to mimic catalytic conditions (illustrated by shaded regions of **Figure 2.8A-B** and summarized in **Table 2.2**). The Ce 3d spectra were fit by ten peaks, where v and u indicate the Ce 3d_{5/2} and Ce 3d_{3/2} spin-

orbit splitting, respectively. The Ce^{4+} oxidation state was identified by three doublets (v/u , v''/u'' , and v'''/u'''), while Ce^{3+} was assigned by a set of doublets (v^0/u^0 and v'/u').⁵⁵ The relative percentages of Ce^{3+} were calculated from the total integrated peak areas of the Ce^{3+} peaks divided by the sum of the integrated peak areas of the Ce^{3+} and Ce^{4+} peaks $\text{Ce}^{3+} (\%) = [A_{\text{Ce}^{3+}} / (A_{\text{Ce}^{3+}} + A_{\text{Ce}^{4+}})] \times 100$. Overall, no direct correlation was observed between the measured Ce^{3+} percent and the presence of dopant for both the samples as-synthesized and after being annealed and treated in catalytic conditions. However, Gd- CeO_2 shows the highest dopant percentage by ICP-OES (15.8%) and the highest Ce^{3+} concentration with respect to dopant (26.6% as-synthesized and 24.8% catalytic conditions). Others have also observed a lack of correlation between the presence of dopant and the Ce^{3+} percentage.⁴⁴ While we anticipated the generation of some Ce^{3+} to correlate with the reduction of Ce^{4+} as a means of charge balancing the presence of M^{3+} in the lattice, it is plausible that the presence of dopants would more directly impact the oxygen vacancies. Furthermore, pre-existing Ce^{3+} in the lattice could be replaced by M^{3+} , potentially explaining why undoped CeO_2 exhibits a relatively higher Ce^{3+} than most of the doped samples. When comparing the Ce^{3+} percentages between the as-synthesized and annealed samples, we observed a consistent decrease in Ce^{3+} percentages. This suggests that after annealing and exposure to water, oxygen diffuses into the lattice and is compensated by oxidation of Ce^{3+} to Ce^{4+} .

Table 2.2. Summary of dopant percentages and Ce^{3+} percentages from XPS spectra and peak intensity ratios from Raman spectra. (^a ICP-OES, ^b XPS, ^c As-synthesized samples, ^d Annealed and dispersed in pH 10 water)

Sample	M^{3+} dopant (%) ^a	M^{3+} dopant (%) ^b	Ce^{3+} (%) ^c	Ce^{3+} (%) ^d	$\text{I}_{560}/\text{I}_{460}$	$\text{I}_{600}/\text{I}_{460}$	$\text{I}_{560}/\text{I}_{600}$
CeO_2	—	—	22.7	16.2	0.022	0.024	0.95
In- CeO_2	9.5	11.7	16.4	13.9	0.069	0.074	0.93
Cr- CeO_2	11.8	17.5	12.5	6.9	0.066	0.080	0.83
Y- CeO_2	15.0	28.5	18.2	11.2	0.144	0.179	0.80
Gd- CeO_2	15.8	18.6	27.3	24.8	0.127	0.148	0.86

We employed Raman spectroscopy to directly probe oxygen vacancies in the annealed CeO₂ after exposure to basic water, as it represents the surface exposed during catalysis.^{44,56,57,58,59,42} The symmetric F_{2g} breathing mode of the 8-fold coordination sphere of O atoms around a Ce cation (CeO₈-type complex) typically appears around 465 cm⁻¹ in the bulk fluorite lattice of ceria (**Figure 2.8C**).^{60,61,62} Because this band primarily reflects the polarization of the O atoms around a central cation, the influence of cation identity, such as electron density and mass, when replacing Ce with dopants is minimal.⁶⁰ Hence, despite the mass differences of Y (37% lighter than Ce) and Gd (12% heavier than Ce), the spectra show only slight shifts (~2 cm⁻¹) to lower frequency in the doped samples. The most significant shift is observed for the Cr-CeO₂, which exhibits asymmetric broadening and a shift to 448 cm⁻¹. This is consistent with previous observations of Cr doping in CeO₂ and its smaller ionic radius, the higher lattice strain induced by Cr, and the overall decrease in nanoparticle size.^{63,64, 65}

After doping CeO₂, we observed the emergence of two additional bands at approximately 560 cm⁻¹ and 600 cm⁻¹, indicative of defects formed by the M³⁺ dopants in the lattice.^{62,60,44,56,42,66,67,68} Prior studies have assigned the band at ~600 cm⁻¹ to a defect in the lattice where a Ce cation is replaced by a dopant M³⁺ without an O²⁻ vacancy, maintaining O_h symmetry, also known as an MO₈-type complex.^{56,44,68} However, the band at ~560 cm⁻¹ is attributed to a defect with an O²⁻ vacancy. We characterized the relative ratios of these defects by evaluating the band intensities at 560 cm⁻¹ (*I*₅₆₀) and 600 cm⁻¹ (*I*₆₀₀) normalized by the band intensity at 460 cm⁻¹ (*I*₄₆₀).⁴⁴ The relative ratios, reported in **Table 2.2** and depicted in the overlaid Raman spectra in **Figure 2.9**, reveal two regimes of oxygen vacancies across the samples. The In-CeO₂ and Cr-CeO₂ yield similar oxygen vacancy ratios, while Gd-CeO₂ and Y-CeO₂ yield similar oxygen vacancy ratios that are larger by a factor of ~2. As anticipated, the oxygen vacancy ratios are more directly correlated to the concentration of the M³⁺ dopant than the Ce³⁺ percentage (**Figure 2.10**).

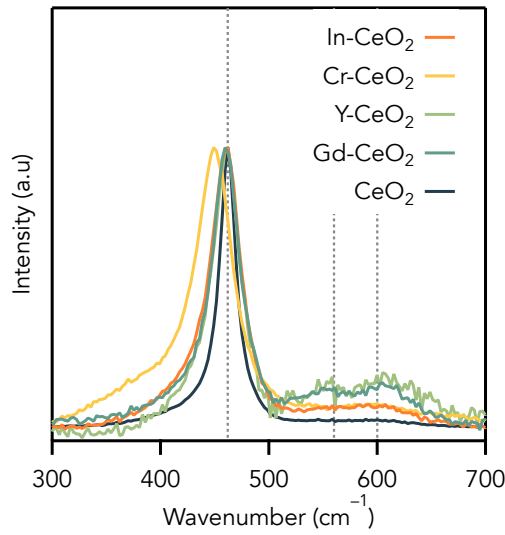


Figure 2.9. Overlaid Raman spectra of all samples with dashed lines indicating the relative intensities at 460 cm^{-1} , 560 cm^{-1} , and 600 cm^{-1} .

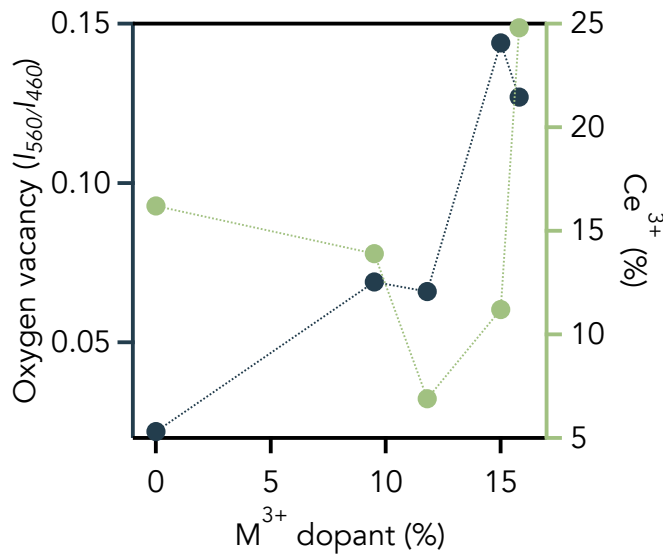


Figure 2.10. Oxygen vacancy ratio (I_{560}/I_{460}) and Ce³⁺ percentage vs. total dopant percentage (ICP-OES).

We attribute the higher Y-CeO₂ oxygen vacancy ratio and a higher percentage of Y³⁺ on the surface by XPS to reflect the effect of oxygen vacancy clustering.^{44,69,70} This phenomenon has been observed in previous studies, where Y³⁺ dopants exceeding 10–15% concentration led to oxygen vacancy clustering

with Y^{3+} on the surface.^{44,71} As described by Mori et al., the formation of microdomains also results in minimizing strain in the lattice.⁷¹ We also observe that Y-CeO₂, which is expected to exhibit a positive tensile strain, has a negative strain close to In-CeO₂.⁶⁹ This observation is further corroborated by the I_{600}/I_{460} ratio, indicating a relatively larger concentration of MO₈-type complexes near the surface in Y-CeO₂ compared to the other doped samples. Conversely, Cr-CeO₂ and In-CeO₂, with lower total M^{3+} concentrations, display slight differences in MO₈-type complexes near the surface, likely a reflection of both the difference in total dopant concentration (ICP-OES) and surface dopant concentration (XPS).

Lastly, examining the I_{560}/I_{600} ratio elucidates the interplay between the M^{3+} dopant, the relative oxygen vacancies, and their spatial arrangement at the surface versus the nanoparticle interior. At unity, there are approximately equal vacancies to dopants near the surface. In undoped CeO₂, we interpret the values for oxygen vacancies to stem from inherent Ce^{3+} in the material. However, the physical meaning of the I_{600} peak value and the corresponding I_{560}/I_{600} should not be overinterpreted and may reflect a baseline level of intrinsic defects. In-CeO₂, which is doped below 10%, reflects a state where M^{3+} and associated oxygen vacancies exist in roughly equal proportions. We hypothesize that the mixture and position of dopants to vacancies is relatively uniform near the surface, with a vacancy close to In^{3+} or Ce^{3+} . Both Cr-CeO₂ and Gd-CeO₂ are observed to have fewer oxygen vacancies per MO₈-type complex ($I_{560}/I_{600} = 0.83$ and 0.86 , respectively), suggesting a less uniform surface where the vacancies are not localized near M^{3+} or Ce^{3+} on the surface and may be more internal. Y-CeO₂ shows the most pronounced unbalance in the I_{560}/I_{600} ratio ($I_{560}/I_{600} = 0.80$), likely due to the formation of microdomains of trivalent Y^{3+} and oxygen vacancies in the lattice.

2.2.3 Hydrolysis of Dimethyl-*p*-nitrophenyl Phosphate

Considering what we have learned about the complex surface of the M-CeO₂ samples, we investigated their impact on organophosphate hydrolysis. The hydrolysis of DMNP, our model organophosphate, was assessed by dispersing CeO₂ nanoparticles into an aqueous N-ethylmorpholine (NEM) solution at pH 10, followed by injection of DMNP dissolved in methanol. The reaction progress was monitored by absorption

spectroscopy at room temperature for the production of the non-toxic byproduct *p*-nitrophenol (*p*-NP, λ_{max} 400 nm) over six and approximately 24 hours (**Figure 2.11**). Percent DMNP conversion was calculated assuming a 1 to 1 mol correspondence between DMNP and *p*-NP based on a calibration curve under identical catalysis conditions (**Figure 2.12–2.13**). As seen in **Figure 2.11B**, the absorbance feature at ~ 270 nm attributed to DMNP decreases as *p*-NP forms over six hours, reaching a plateau by 24 hours. A shoulder feature around 290 nm corresponds to CeO_2 .⁷² Control experiments conducted without NEM for pH correction and without CeO_2 catalyst resulted in $\sim 5\%$ and $\sim 8\%$ product formation after 24 hours, respectively (**Figure 2.14–2.15**). Our choice of NEM was guided by prior publications that used this model system to measure organophosphate degradation.^{18,73,74,4}

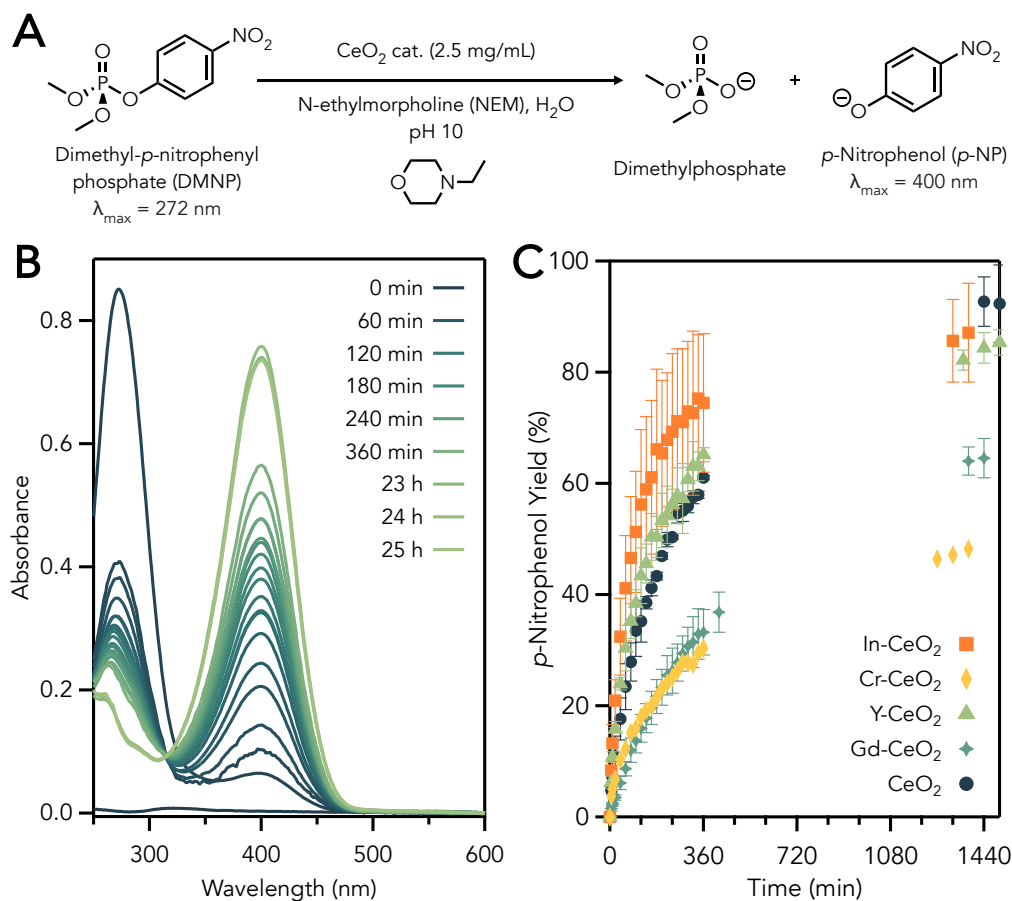


Figure 2.11. (A) Scheme of DMNP degradation reaction, (B) UV–visible absorption spectra of reaction aliquots, and (C) DMNP conversion to *p*-NP over time.

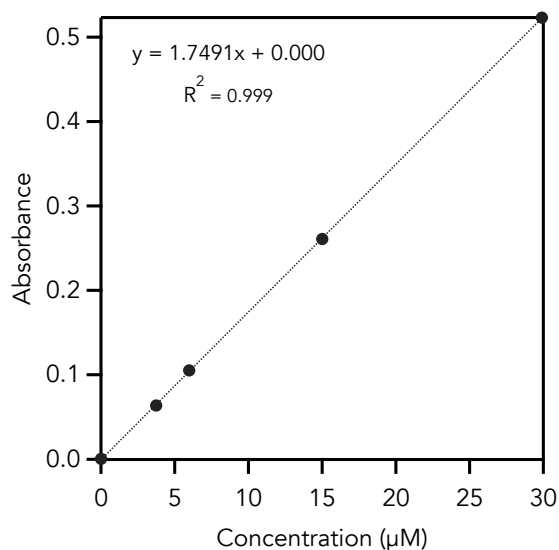


Figure 2.12. Calibration curve of *p*-nitrophenol in 80 mM NEM (pH = 10).

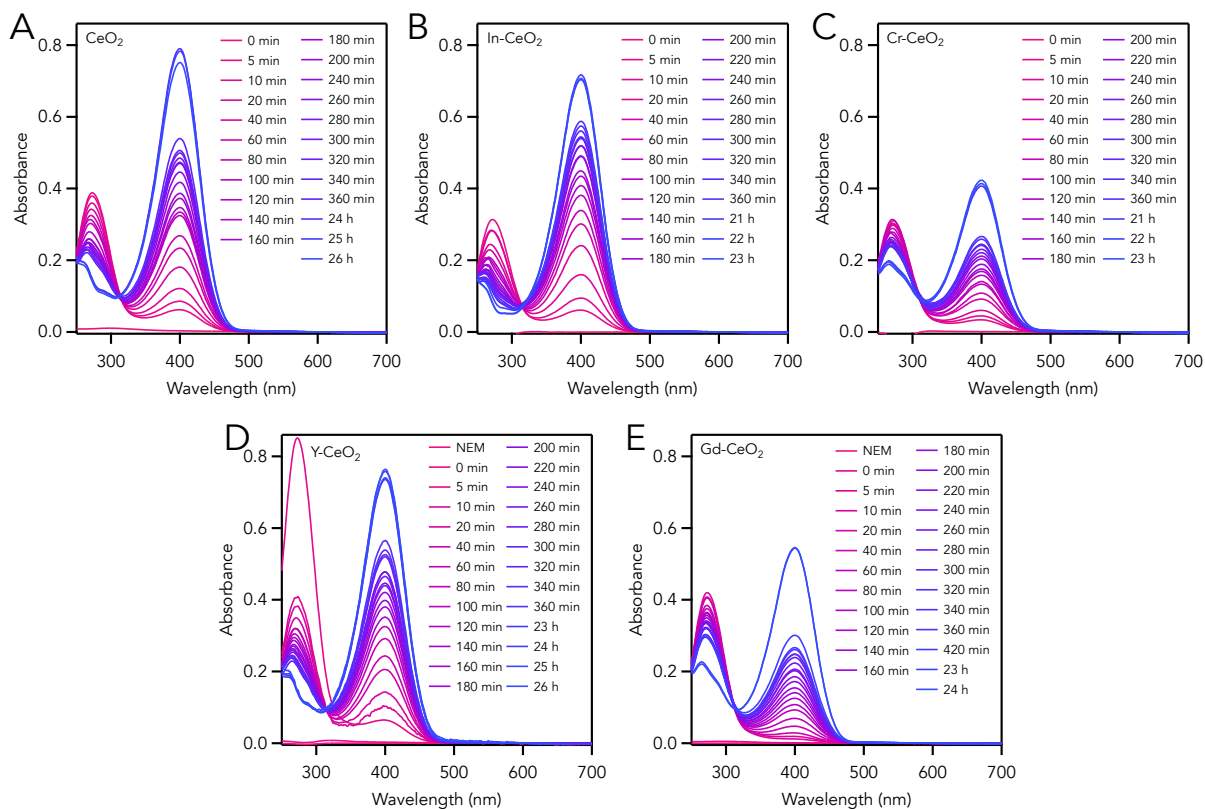


Figure 2.13. Representative UV-vis traces tracking DMNP hydrolysis for (A) CeO₂, (B) In-CeO₂, (C) Cr-CeO₂, (D) Y-CeO₂, (E) Gd-CeO₂.

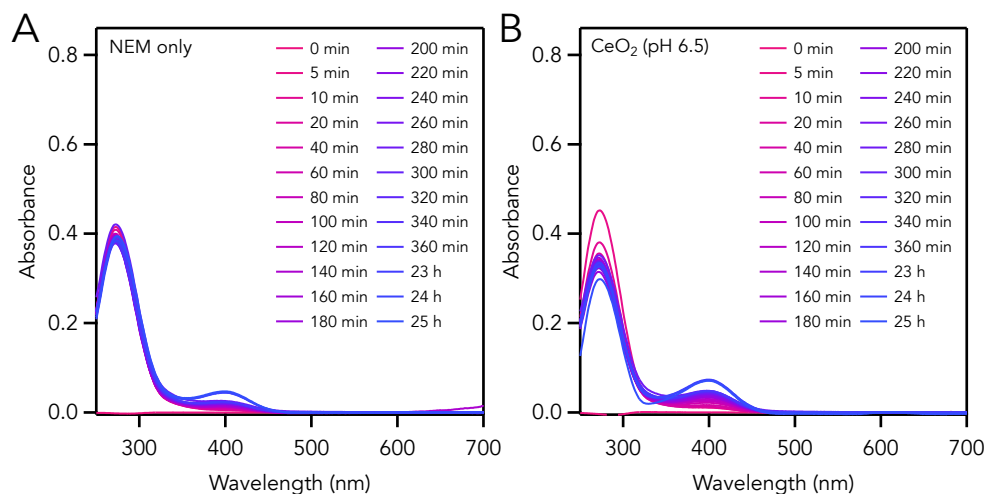


Figure 2.14. UV-vis traces tracking DMNP hydrolysis for controls with (A) NEM buffer only and (B) CeO₂ (DI H₂O, pH 6.5).

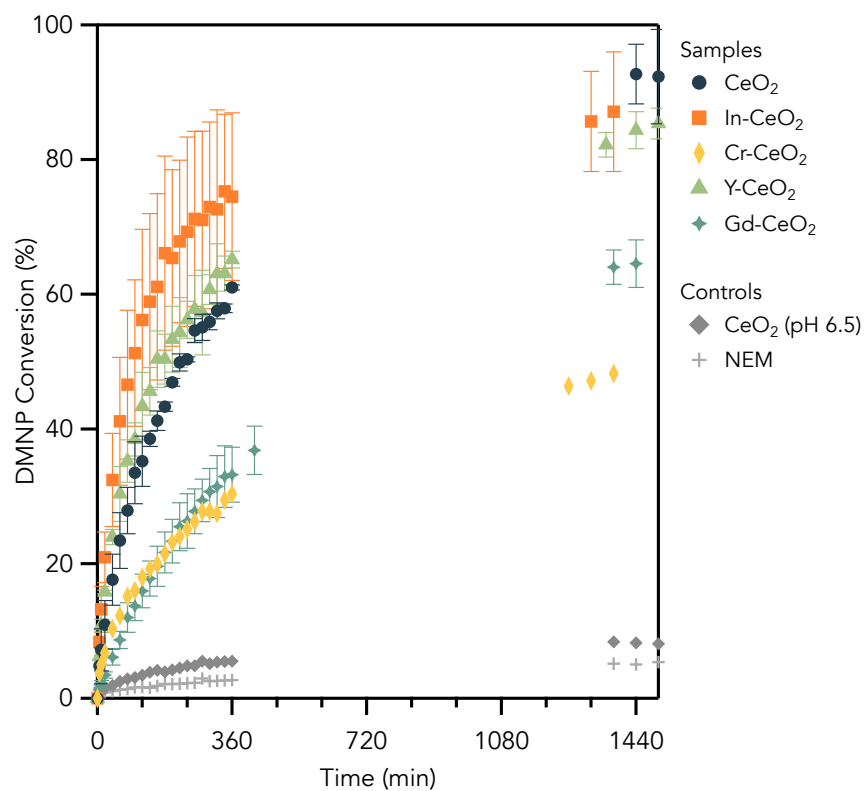


Figure 2.15. DMNP conversion of all samples including control experiments with CeO₂ and no pH correction (grey diamond), and NEM pH correction and no CeO₂ (grey plus sign).

Table 2.3. Summary of rate $k_{obs,6h}$ and percent conversion after six hours for all samples. (^a calculated from initial 40 mins)¹⁸

Sample	$k_{obs,6h} (\times 10^{-3} \text{ min}^{-1})$	Initial Rate ($\mu\text{M min}^{-1}$) ^a	Conversion @ 6h (%)
CeO ₂	2.49 ± 0.21	103 ± 17	61.0 ± 0.4
In-CeO ₂	3.88 ± 1.50	191 ± 39	75 ± 12
Cr-CeO ₂	0.91	57.5	30.3
Y-CeO ₂	2.63 ± 0.38	141 ± 11	65 ± 1
Gd-CeO ₂	1.12 ± 0.16	36 ± 6	33 ± 4
No catalyst	0.07	5.3	2.7

Table 2.3 summarizes the first-order observed kinetic rate ($k_{obs,6h}$) obtained by fitting the first 6 hours of the reaction and the initial rate based on the concentration of *p*-NP produced in the first 40 mins.¹⁸ As depicted in **Figure 2.16A**, comparing doped to undoped CeO₂ reveals that In-CeO₂ has a greater initial rate and $k_{obs,6h}$ compared to CeO₂ by a factor of approximately 1.5. In contrast, Cr-CeO₂ and Gd-CeO₂ samples have lower rates than CeO₂ by a factor of about 0.5. We attribute this difference in activity to the complex interplay of structural and defect-based disparities, as discussed above. Specifically, Cr-CeO₂ and Gd-CeO₂ display relatively higher surface strain (-1.2×10^{-3} and 2.7×10^{-3} , respectively) as compared to the CeO₂, Y-CeO₂, and In-CeO₂, which maintain strain values closer to zero (**Figure 2.16B**). This difference in strain may impact the adsorption and proximity of the substrate and water/ $-\text{OH}$ molecules required to perform hydrolysis. Several prior publications have investigated the direct correlation of nanoparticle size, surface area, oxygen vacancy content, and Ce^{3+} concentration on the adsorption ability of $-\text{OH}$ and substrate.^{32,34} In the case of Ederer et al., they found that an intermediate level of nanoparticle size and surface area yielded optimal adsorption conditions.³⁴ Our samples reveal a similar optimization of nanoparticle size and

strain for best catalytic activity, As depicted in **Figure 2.16C**, while reactivity does not linearly track with % Ce^{3+} , there may be an inhibitory effect on catalysis beyond a certain threshold of Ce^{3+} , given the lower Lewis acidity of Ce^{3+} compared to Ce^{4+} ($\text{Ce}^{4+} pK_a = -1.15$ and $\text{Ce}^{3+} pK_a = 9.3$), thereby limiting available sites for DMNP adsorption, which requires a Lewis acidic Ce^{4+} .^{3,5,53}

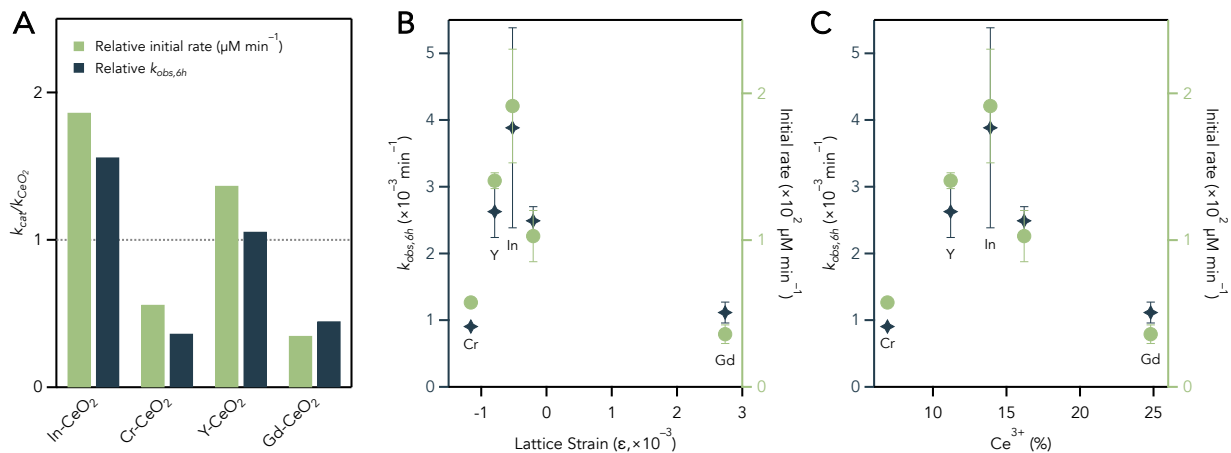


Figure 2.16. DMNP degradation catalyzed by M-CeO₂: (A) Relative rate of catalyst normalized by undoped CeO₂ and (B) comparisons of activity with respect to lattice strain (C) and Ce^{3+} percentage.

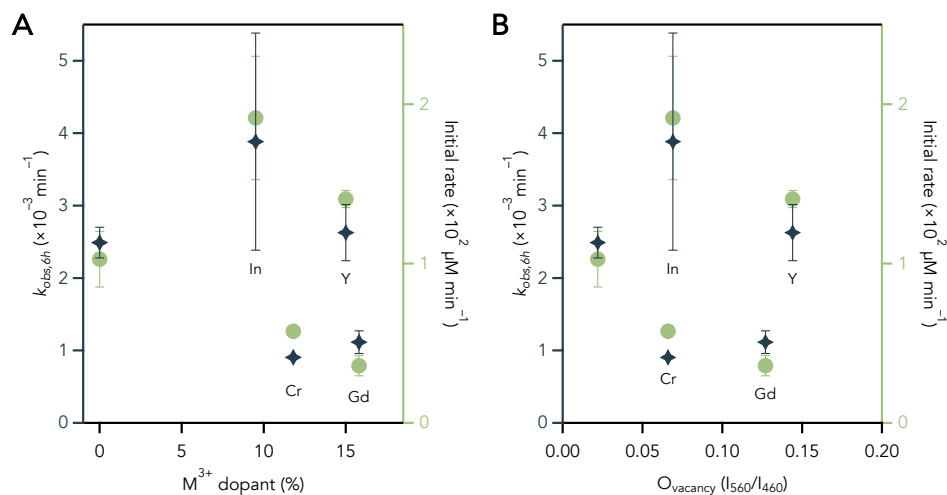


Figure 2.17. Rates of reaction with respect to (A) total M^{3+} dopant concentration and (B) oxygen vacancy ratio (I_{560}/I_{460}).

Based on the proposed mechanism,^{6,18,42} elimination of the hydrolysis products requires proximity of adsorbed substrate to adsorbed –OH, which is influenced by the position and concentration of oxygen vacancies. However, while previous studies have directly correlated oxygen vacancies and reactivity, we do not observe a direct relationship with our samples (**Figure 2.17**).^{5,42,75,41} Despite In-CeO₂ not exhibiting the highest relative oxygen vacancy content, we hypothesize that it performed the best as a catalyst due to its ability to balance multiple catalytic requirements: having a defect surface with Ce⁴⁺ (Lewis acidic site for DMNP adsorption),³ In³⁺/Ce³⁺ with oxygen vacancies, and coordinated –OH near the Ce⁴⁺ with adsorbed substrate, along with low overall surface strain. Y-CeO₂ demonstrated the highest oxygen vacancy content, yet relative to CeO₂ and In-CeO₂, it had a significantly greater amount of Y³⁺ on the surface, which has a *pK_a* of ~8.3, which is akin to having more Ce³⁺ on the surface like undoped CeO₂, hence their similarity in catalysis.⁵²

One significant challenge in working with annealed CeO₂ nanoparticles for catalysis is their lack of colloidal stability. Heterogeneous catalysts tend to have more considerable variability in repeat measurements⁷⁵ and decreased accessible surface area due to particle aggregation. One approach to improving the dispersion of CeO₂ is introducing ligand additives or polymeric membranes. We briefly explored the use of poly-*N*-substituted glycines (peptoids), which are sequence-defined biomimetic polymers functionalized with binding headgroups that coordinate to metal oxide surfaces such as carboxylates and catecholates.⁷⁶ These tunable polymers readily self-assemble into crystalline nanosheets, and these self-assembled peptoid sheets have previously been demonstrated to disperse metal ions to create a membrane-like surface for DMNP hydrolysis.⁴ In testing their addition to our system (see **Figure 2.18–2.19**), we observed a 25% and 24% increase in *k_{obs}* using a peptoid sheet additive compared to peptoid monomers in solution for the carboxylate and catecholate binding groups respectively. While these additives overall tended to decrease reactivity compared to native CeO₂, we are optimistic that with further optimization, using peptoids as a membrane scaffold may be useful in heterogeneous catalysis.

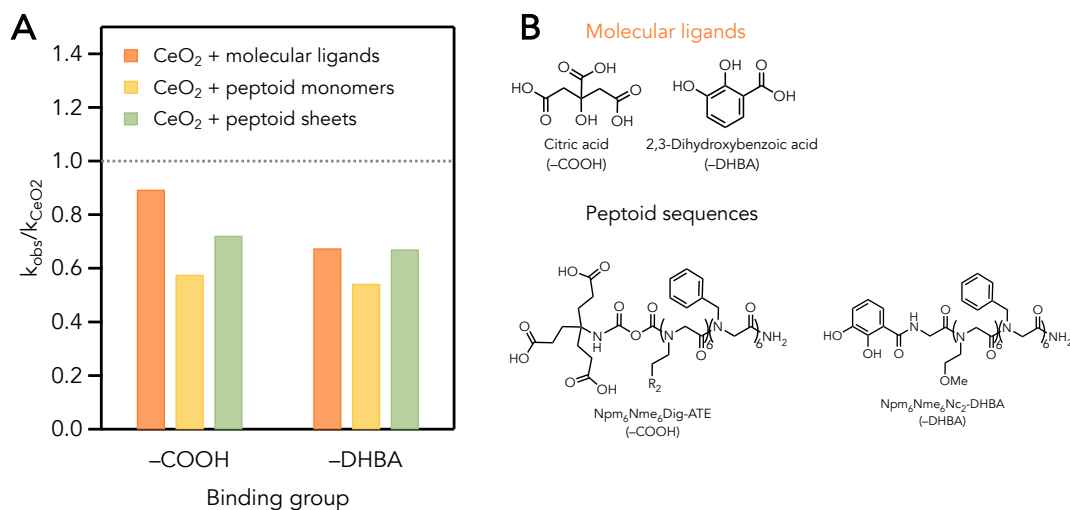


Figure 2.18. Testing catalytic activity of undoped CeO_2 with additive molecular ligands and peptoid sequences. (A) Relative rates compared to CeO_2 of CeO_2 mixed with 0.01 equiv. (with respect to 1 equiv. DMNP) of molecular ligands, peptoid monomers (sequences dissolved in 1:1 MeCN/ H_2O solution), and peptoid sheets (sequences assembled overnight in a 1:1 MeCN/ H_2O solution). (B) Molecular ligands and peptoid sequences with carboxylate (-COOH) and catechol (-DHBA) binding groups.

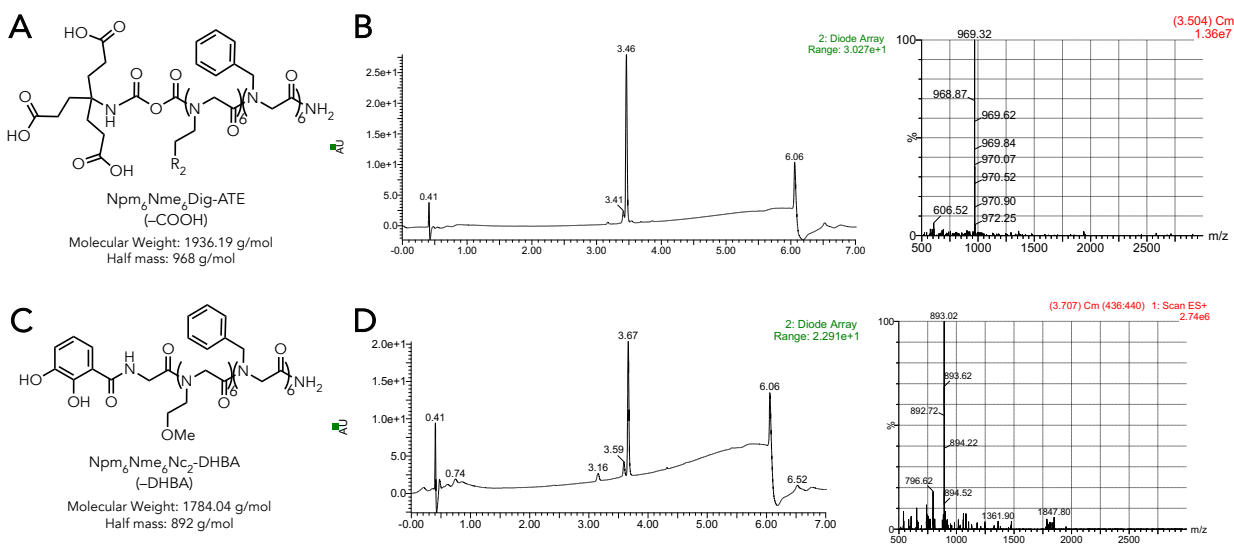


Figure 2.19. UPLC characterization of carboxylate peptoid ($Npm_6Nme_6DigATE$) and catechol peptoid ($Npm_6Nme_6Nc_2DHBA$) sequences showing (A and C respectively) structure, and (B and D respectively) LC-MS chromatogram with associated ESI⁺ ionization pattern.

2.3 Conclusion

In conclusion, we have demonstrated the successful doping of CeO₂ with Y³⁺, Cr³⁺, In³⁺, and Gd³⁺ via a straightforward hydrothermal method. We investigated the influence of dopants with different ionic radii and pK_a values on dopant incorporation and defect structures in CeO₂. Our investigation revealed that the dephosphorylation of DMNP, a model organophosphate substrate, was impacted by multiple changing features of the CeO₂ surface, including the concentration and dispersion of oxygen vacancies. Specifically, our findings underscore the intricate interplay of various factors—including the Ce³⁺/Ce⁴⁺ ratio, presence of oxygen vacancies, lattice strain, and the relative proximities of Ce⁴⁺ to oxygen vacancies and Ce³⁺—in shaping an active site ensemble conducive to efficient catalysis, emphasizing the critical importance of understanding the dynamic role of active site ensembles in catalytic processes.⁷⁷ Despite the inherent challenges and variability of heterogeneous catalysis,⁷⁵ our results present a self-contained snapshot of the broader landscape of heterogeneous CeO₂ catalysis and identify the critical factors of CeO₂ surface defects that impact organophosphate hydrolysis. The conclusions from this work may further our understanding of heterogeneous catalysis at the surface of nanocrystalline CeO₂.

2.4 Experimental Methods

2.4.1 General Methods and Materials

All synthetic preparations and catalysis experiments were performed in ambient air in a well-ventilated fumehood or on a benchtop unless otherwise stated. All chemicals listed below were used without further purification unless stated otherwise. Cerium(III) nitrate hexahydrate ($\geq 99\%$ trace metals basis), yttrium(III) nitrate hexahydrate ($\geq 99.8\%$ trace metals basis), chromium(III) nitrate nonahydrate ($\geq 99.9\%$ trace metals basis), indium(III) nitrate hydrate ($\geq 99.99\%$ trace metals basis), gadolinium nitrate hexahydrate ($\geq 99.9\%$

trace metals basis), *tert*-butylamine ($\geq 99.5\%$), toluene (ACS reagent, $\geq 99.5\%$), hexanes (ReagentPlus, $\geq 99\%$), ethanol (200 proof, anhydrous, $\geq 99.5\%$), and methanol (ACS reagent, $\geq 99.8\%$) were all purchased from Millipore Sigma. Oleic acid (99%) and *N*-ethylmorpholine (98%) was purchased Thermo Fisher Scientific. Dimethyl-*p*-nitrophenyl phosphate (98.9%) was purchased from Santa Cruz Biotechnology. All DI water used was 18.2 M Ω water collected from an EMD Millipore purification system.

For peptoid synthesis all chemicals were obtained from Millipore Sigma or Thermo Fisher and used without further purification. 4-(2',4'-Dimethoxyphenyl-Fmoc-aminomethyl)-phenoxy resin (Rink amide resin, Novabiochem), 4-methylpiperidine (PIP), dimethylformamide (DMF), bromoacetic acid, *N,N*-diisopropylethylamine (DIC), *N*-methyl-2-pyrrolidone (NMP), benzylamine, β -alanine, and 2-methoxyethylamine, Fmoc-gly-OH, 2,3-dihydroxybenzoic acid (DHBA), hydroxybenzotriazole (HOBt), tetrahydrofuran (THF), dichloromethane (DCM), trifluoroacetic acid (TFA), diglycolic anhydride, 4-dimethylaminopyridine (DMAP), pyridine, 3-[bis(dimethylamino)methyl]iumyl]-3*H*-benzotriazol-1-oxide hexafluorophosphate (HBTU), *N,N*-diisopropylethylamine (DIPEA), di-*tert*butyl-4-amino-4-(3-*tert*-butoxy)-3-oxopropyl)heptanedioate (ATE).

2.4.2 Instrumentation and Characterization Methods

Transmission electron microscopy (TEM) images were obtained with a FEI Tecnai G2 F20 SuperTwin microscope operated at 200 kV using bright field imaging. *As-synthesized* samples were prepared by drop-casting 5 μ L of sample dissolved in hexanes onto a suspended ultrathin carbon film on lacey carbon support film, 400 mesh, copper grids purchased from Ted Pella, Inc. The samples were allowed to dry in air for 5 min until the hexanes evaporated. All grids were placed under vacuum overnight to ensure complete dryness before imaging.

Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 Discover diffractometer at 50 kV with 1000 μ A via a Cu anode microfocus X-ray source ($\lambda = 1.5406 \text{ \AA}$) and a Pilatus 100K large-area detector. The beam for the measurement was collimated to a 1 mm beam diameter, and collection times were 30–90 s per step (5.5° 2 θ step size). Raw diffraction data were processed using Bruker DIFFRAC.EVA

software, and peaks were fitting with Pseudo-Voigt multipeak functions using Python. *As-synthesized* samples were prepared by repeatedly drop-casting 5 μL of sample suspended in hexanes onto a Si wafer to build up a thick film of sample. *Annealed* samples were prepared by repeatedly drop-casting 5 μL of sample suspended in DI water onto a Si wafer to build up a thick film of sample.

Thermogravimetric analysis (TGA) data were collected on a TA Instruments TGA Q5000 under N_2 (g) at a scan rate of $10^\circ\text{C}/\text{min}$.

Annealing was performed in a quartz tube using a Lindberg/Blue M Mini-Mite Tube Furnace with a continuous N_2 (g) flow at 500°C for 10 min (ramp rate too 500°C : $10^\circ\text{C}/\text{min}$), see *Preparation of nanoparticles for catalysis* for more details on annealing.

Elemental analysis was performed by inductively coupled plasma-optical emission spectroscopy (ICP–OES) on a Perkin Elmer Optima 3000. Samples were digested for 48 h in a 1:1 conc. $\text{H}_2\text{O}_2/\text{conc. HNO}_3$ then filtered and diluted to 2% HNO_3 for analysis.

X-ray photoelectron spectroscopy (XPS) data were taken on a Kratos Axis-Ultra DLD spectrometer. This instrument has a monochromatized $\text{Al K}\alpha$ X-ray and a low energy electron flood gun for charge neutralization. X ray spot size for these acquisitions was on the order of $700 \times 300 \mu\text{m}$. The electrostatic lens was used for data collection. Pressure in the analytical chamber during spectral acquisition was less than 5×10^{-9} Torr. Pass energy for survey spectra (composition) was 160 eV. Pass energy for the high-resolution spectra was 40 eV. The take-off angle (the angle between the sample normal and the input axis of the energy analyzer) was 0° (0-degree take-off angle $\sim 100 \text{ \AA}$ sampling depth). The Kratos Vision2 software program was used to determine peak areas and to calculate the elemental compositions from peak areas. CasaXPS was used to peak fit the high-resolution spectra. For the high-resolution spectra, a Shirley background was used, and all binding energies were referenced to the C 1s C-C bonds at 285.0 eV. *As-synthesized* samples were prepared by repeatedly drop-casting 5 μL of sample suspended in hexanes onto a Si wafer to build up a thick film of sample. *Annealed* samples were prepared by repeatedly drop-casting 5 μL of sample suspended in DI water via sonication onto a Si wafer to build up a thick film of sample.

Raman spectroscopy measurements were performed using a Renishaw InVia equipped with a Leica DMIRBE inverted optical microscope and a 514 nm excitation source. *Annealed* samples were prepared by drop-casting 5 μ L of sample suspended in water onto a Si wafer. Raman spectra were collected at three to five different areas in each material to represent the average surface.

UV-visible (UV-vis) absorption spectroscopy kinetics data were collected on an Agilent Cary 60 UV-vis spectrophotometer with an Agilent xenon source lamp. All UV-vis data was collected at 1 nm/min scan rate from 800 nm to 250 nm.

For purification and characterization of peptoids: Purification was performed by reverse-phase High-Performance Liquid Chromatography (HPLC) on an XBridge Prep C18 OBDTM column (10 μ m, 19 mm $\times$ 100 mm) using a narrow gradient of MeCN in H₂O. Purity was analyzed using a Waters ACQUITY reverse-phase Ultra-Performance Liquid Chromatography (UPLC) and connected Waters SQD2 mass spectrometry system.

2.4.3 *Synthesis of CeO₂ Nanoparticles*

As described by Yang and Gao,⁴⁵ cerium(III) nitrate (0.25 mmol, 1 equiv., 0.1088 g) as dissolved in 15 mL of DI water (16.7 mM) and transferred to a 50 mL Teflon-lined stainless-steel autoclave. In a separate vial, 15 mL toluene, 1.5 mL oleic acid, and 0.15 mL *tert*-butyl amine were combined and added to the autoclave. The autoclave was sealed in ambient air in the fumehood and transferred to a 180°C oven, then held at 180°C for 24 h. At 24 h, the autoclave was removed from the oven and allowed to cool in the fumehood to room temperature. The crude solution was a bilayer containing a dark brown toluene layer containing the CeO₂ nanoparticle product and a bottom clear water layer. The reaction mixture was purified by a series of centrifugation steps. First, the crude reaction mixture was transferred to a Falcon tube for centrifugation at 10000 rpm for 10 min, crashing out solid impurities. Then, the toluene layer was decanted from the water layer into a clear Falcon tube. The toluene layer (~15 mL) was precipitated using 5-10 mL of ethanol until precipitation and the precipitated particles were isolated by centrifugation. The supernatant (typically a clear light brown on the first crash out) was poured off and the pellet was redissolved in toluene

to be precipitated twice more. The final pellet was redissolved/resuspended in hexanes. Sometimes, the purification process causes a slight stripping of the oleic acid ligands, and the particles lose colloidal stability by the third precipitation step. The particle solution/suspension in hexanes is used for TEM sample preparation, XPS sample preparation, and XRD sample preparation. However, because the ligands were removed completely during annealing, we found it more important to ensure all impurities were removed via centrifugation even if it did cause this instability.

2.4.4 *Synthesis of M-doped CeO₂ Nanoparticles (M = Y, Cr, In, Gd)*

As adapted from Yang and Gao,⁴⁵ a combination of cerium(III) nitrate (0.212 mmol, 0.85 equiv., 0.092 g) and the corresponding metal nitrate salt, yttrium(III) nitrate hexahydrate (0.038 mmol, 0.15 equiv., 0.014 g), chromium(III) nitrate nonahydrate (0.038 mmol, 0.15 equiv., 0.015 g), anhydrous indium(III) nitrate (0.038 mmol, 0.15 equiv., 0.011 g), or gadolinium(III) nitrate hexahydrate (0.038 mmol, 0.15 equiv., 0.017 g) was dissolved in 15 mL of DI water (16.7 mM) and transferred to a 50 mL Teflon-lined stainless-steel autoclave. In the case of indium(III) nitrate hydrate, a portion of indium(III) nitrate hydrate was dried at 100°C under vacuum to multiple days to produce the anhydrous salt, which was then weighed out for synthesis. The same procedure as the synthesis of the undoped CeO₂ nanoparticles was followed. One observation of note was that the Cr-CeO₂ samples appeared to yield a noticeably darker brown toluene solution after purification and maintained better colloidal stability than the rest of the samples.

2.4.5 *Preparation of nanoparticles for catalysis*

Annealing of the nanoparticles after purification was performed in a tube furnace with a quartz tube and a continuous N₂ (g) flow. Samples were prepared by drop-casting from a hexanes solution onto aluminum foil wrapped ceramic boats and air-dried using an N₂ flow to leave a thick layer of nanoparticles on the foil. The boats were loaded into the quartz tube. The heating ramped from room temperature to 500°C with a ramp rate of 10°C/min, then held at 500°C for 10 min before cooling to room temperature. The annealed product was isolated from the aluminum foil as a black flaky powder.

2.4.6 Measurement of dimethyl-*p*-nitrophenyl phosphate (DMNP) hydrolysis

The measurement of DMNP hydrolysis was guided by several prior studies.^{18,78,15,73,4} All hydrolysis experiments were performed in 4.5 mL scintillation vials charged with a tiny PTFE egg-shaped stir bar (3/8 x 3/16). A solid sample of annealed CeO₂ nanoparticles (2.5 mg) was added to the vial and suspended in a buffered solution of *N*-ethylmorpholine (NEM, 0.975 mL, 80 mM, pH 10). The suspension was sonicated for 1 h to suspend/disperse the CeO₂ nanoparticle powder as a black/dark brown suspension. While the nanoparticles were sonicating, a stock solution of DMNP (4.47 μ L) in MeOH (20.53 μ L, 25 mM) was prepared to improve the solubility of DMNP upon injection in the reaction mixture. For these UV-vis absorption scans, the instrument was baselined using a blank of NEM buffer solution. After sonication was complete, the vial was placed in the fumehood at room temperature and stirred at 400 rpm for the entire duration of the reaction. An initial (0 min) scan was collected by withdrawing a 4 μ L aliquot of the reaction mixture while stirring, prior to DMNP injection, and diluted to 2 mL using the prepared NEM buffer solution in a quartz cuvette. After DMNP solution (25 μ L) injection, aliquots (4 μ L diluted to 2 μ L with NEM buffer solution) were collected at 5 min, 10 min, 20 min, and every 20 mins following for the following 6 hours. The reaction was allowed to stir overnight, and aliquots were collected at time points from 22 h to 25 h after the start of the reaction.

2.4.7 Synthesis of functionalized peptoids (*Npm*₆*Npm*₆)

As described by prior literature,^{79,80,81,82} rink amide resin (0.09 mmol) was deprotected with addition of 20% v/v PIP/DMF (2 mL), agitation for 40 min, filtering, and washed with DMF (3x). Resins were mixed with 1.5 mL of 0.6 M bromoacetic acid (2 mL) and 50% v/v DIC/DMF (0.3 mL), agitated for 10 min, filtered, and washed with DMF (3x). Nucleophilic displacement occurred by mixing the resins with 1.5 mL of 0.6 M solution primary amine monomers (benzylamine or 2-methoxyethylamine) in NMP, agitation for 10 min, filtering, and washed with DMF (3x). These steps are repeated until the following sequence was achieved: 6 benzylamine submonomer units (*Npm*₆) and 6 2-methoxyethyl submonomer units (*Nme*₆).

2.4.7.1 Functionalization with catecholate: 2,3-dihydroxybenzoic acid ($Npm_6Nme_6Nc_2DHBA$)

Synthesis was adapted from Soulère et al and Fan et al.^{83,84} Npm_6Nme_6 resins (assuming 0.09 mmol) were mixed with Fmoc-gly-OH (10 xs, ~300 mg per 100 mg resin) and 50% v/v DIC/DMF was added. Mixture was agitated overnight, then deprotected with 20% PIP/DMF (2 mL) for 40 min, filtered, and washed with DMF (3x). In a separate vial, DHBA (1.1 eq., 9.8 mg) and HOBt (1 eq., 7.8 mg) were suspended in anhydrous THF (~0.5 mL). DCC (1.2 eq., 14.3 mg) in anhydrous THF (~0.5 mL) was added dropwise to the DHBA solution, then agitated for 15 min under N_2 . Resins were added to DHBA vial, and the whole mixture was degassed with N_2 and agitated 30 min, then washed with DMF (3x) and DCM (3x). Cleavage of the resin was performed using 95% TFA in H_2O (2–3 mL, ~30 min agitation).

2.4.7.2 Functionalization with carboxylate: di-tertbutyl-4-amino-4-(3-tert-butoxy)-3-oxopropyl)heptanedioate (–ATE)

Npm_6Nme_6 resins (assuming 0.09 mmol) were mixed with diglycolic anhydride (1 eq., 104 mg), DMAP (16 mg), pyridine (1 mL) in DCM (2 mL). Solution was agitated overnight, filtered, and washed with DCM (3x). In a separate vial, HBTU (5 eq., 1.7 mg) and DIPEA (10 eq. 1.5 mL) in DMF (1.5 mL) was dissolved together and added to the resins and shaken for 10 min. Then, ATE (5 eq., 1.5 mg) was added and the mixture was agitated overnight, filtered, then washed with DMF (3x) and DCM (3x). Cleavage of the resin was performed with 95% TFA in H_2O (2–3 mL, 5-hour agitation).

2.5 Appendix: X-ray Photoelectron Spectroscopy Data

Ce 3d XPS spectra were fit using reference spectra from Paparazzo et al.'s work on fitting Ce 3d spectra of Ce_2O_3 and CeO_2 .⁵⁴ Y 3d XPS spectra were fit using reference spectra from Barreca et al. and the publicly-accessed Thermo Fisher Yttrium XPS reference.^{85,86} In 3d spectra were fit using Detweiler et al. and the Thermo Fisher Indium XPS reference.^{87,88} Cr 2p spectra were fit using Biesinger et al., Aronniemi et al.,

Salvi et al, and the Thermo Fisher Chromium XPS reference.^{89,90,91,92} Lastly, Gd 4d spectra were fit using reference spectra from Barreca et al., Gupta et al., and Raiser et al.^{93,94,95}

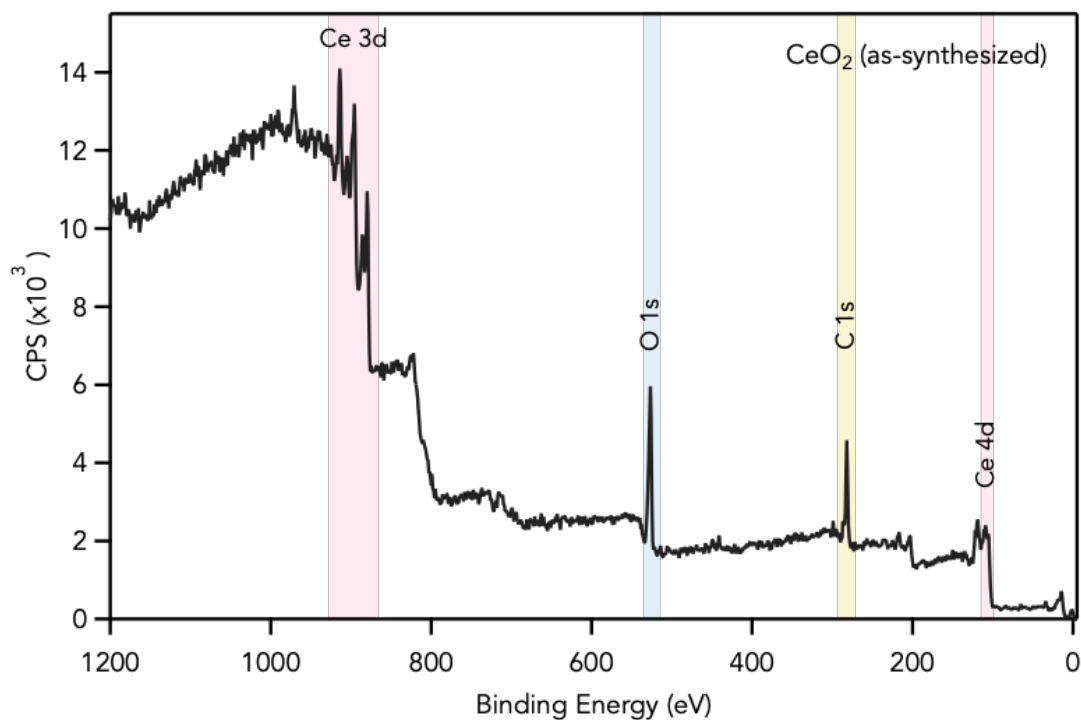


Figure 2.20. XPS survey spectrum of as-synthesized CeO₂.

Table 2.4. XPS survey spectrum composition table of as-synthesized CeO₂.

Peak	Type	Binding Energy (eV)	Atomic %
Ce	3d	896	14.46
O	1s	527	35.28
In	3d	441	0.22
C	1s	282	50.04

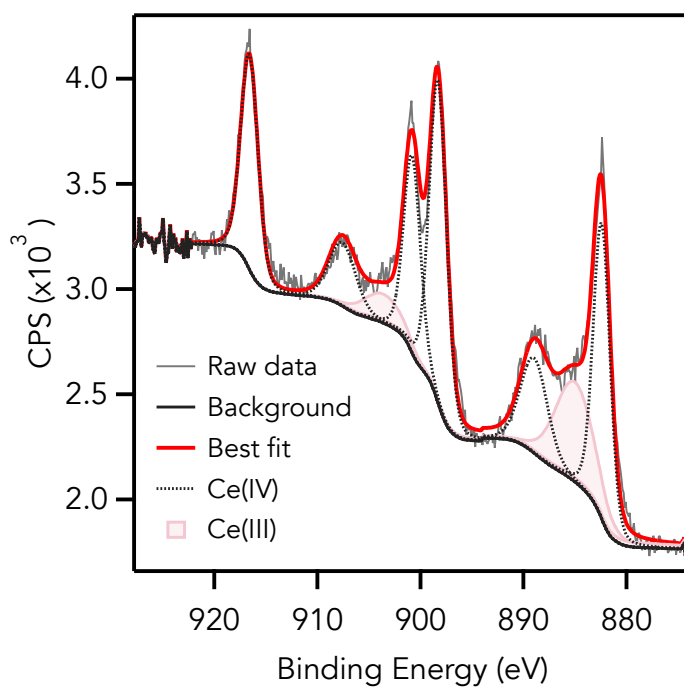


Figure 2.21. High resolution Ce 3d XPS spectrum of as-synthesized CeO₂.

Table 2.5. High resolution Ce 3d XPS fitting components of as-synthesized CeO₂.

Name	Ce(IV)						Ce(III)			
	v	u	v''	u''	v'''	u'''	v^0	u^0	v'	u'
Position	882.4	900.8	889.0	907.6	898.3	916.6	881.0	899.3	885.0	903.6
FWHM	1.93	1.93	3.09	3.09	1.99	1.99	19.38	19.38	4.49	4.49
Area	3105.51	2070.34	1599.6	1066.4	3489.54	2326.36	520.62	347.08	2441.96	708.54

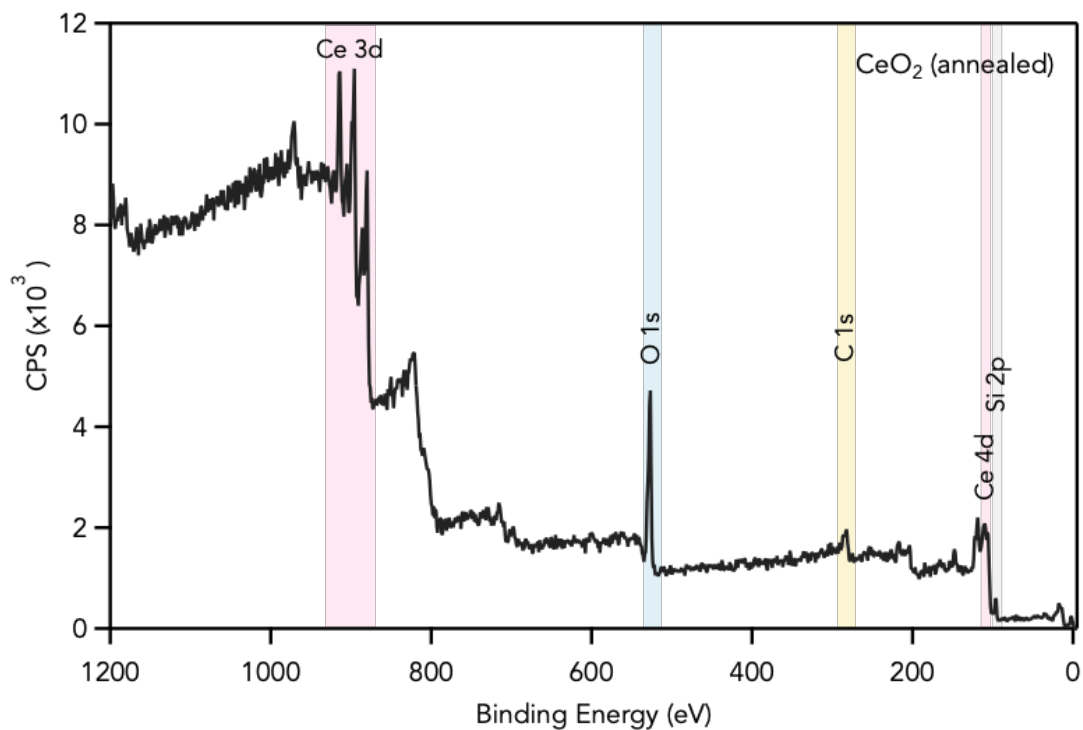


Figure 2.22. XPS survey spectrum of annealed CeO₂.

Table 2.6. XPS survey spectrum composition table of as-synthesized CeO₂.

Peak	Type	Binding Energy (eV)	Atomic %
Ce	3d	896	22.6
O	1s	527	48.7
C	1s	282	23.3
Si	2p	96	5.5

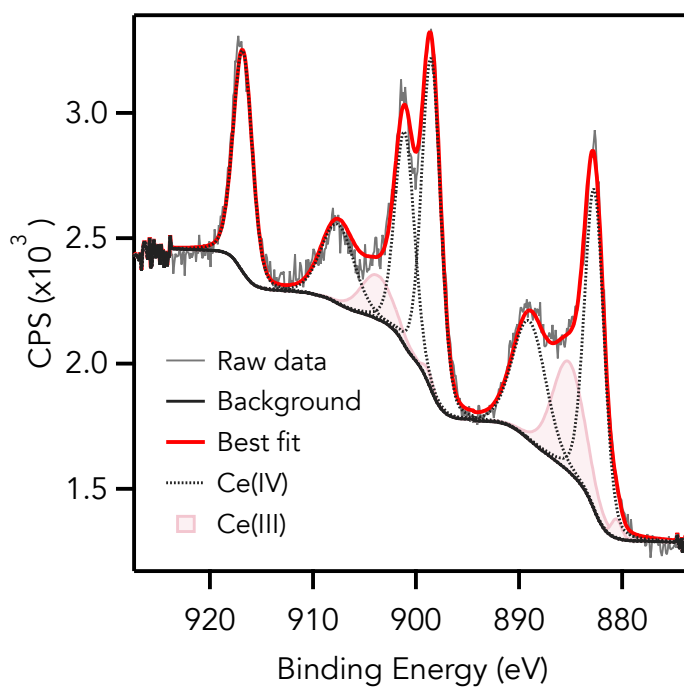


Figure 2.23. High resolution Ce 3d XPS spectrum of annealed CeO₂.

Table 2.7. High resolution Ce 3d XPS fitting components of as-synthesized CeO₂.

Name	Ce(IV)						Ce(III)			
	ν	u	ν''	u''	ν'''	u'''	ν^0	u^0	ν'	u'
Position	882.7	901.1	889.0	907.6	898.5	916.8	880.6	898.9	885.2	903.8
FWHM	2.22	2.22	3.78	3.78	2.17	2.17	1.18	1.18	3.69	3.69
Area	3258.67	2172.45	2055.84	1370.56	3294.20	2196.13	104.34	69.56	1853.42	741.27

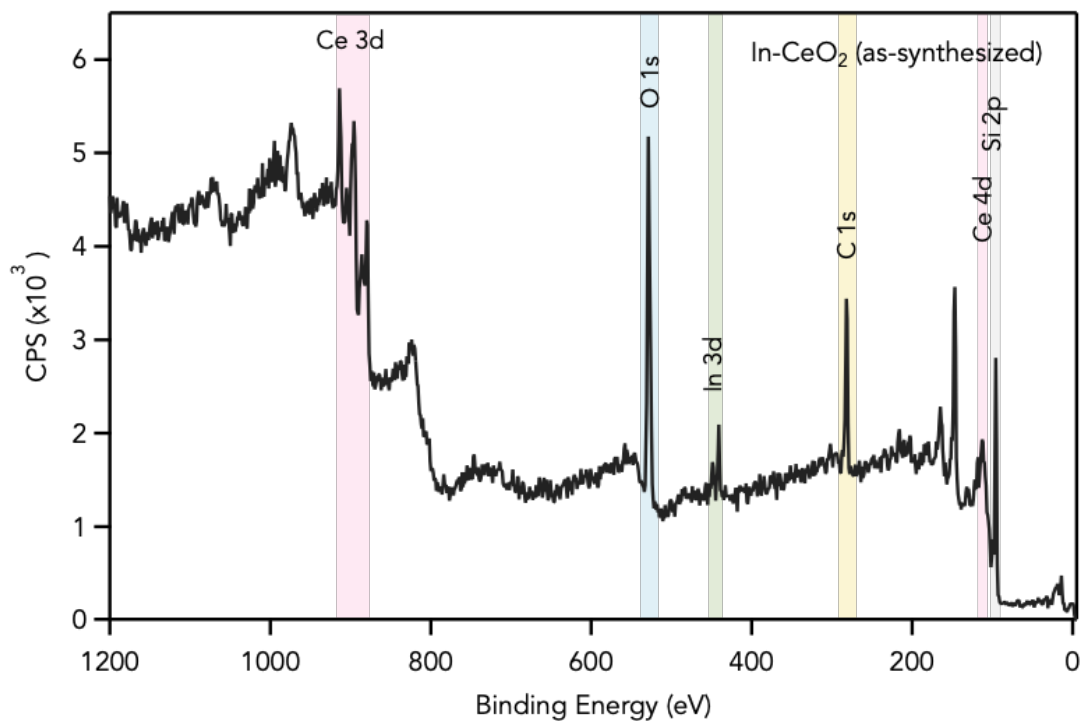


Figure 2.24. XPS survey spectrum of as-synthesized In-CeO₂.

Table 2.8. XPS survey spectrum composition table of as-synthesized CeO₂.

Peak	Type	Binding Energy (eV)	Atomic %
Ce	3d	896	6.1
O	1s	529	33.0
In	3d	441	0.8
C	1s	282	31.9
Si	2p	96	28.1

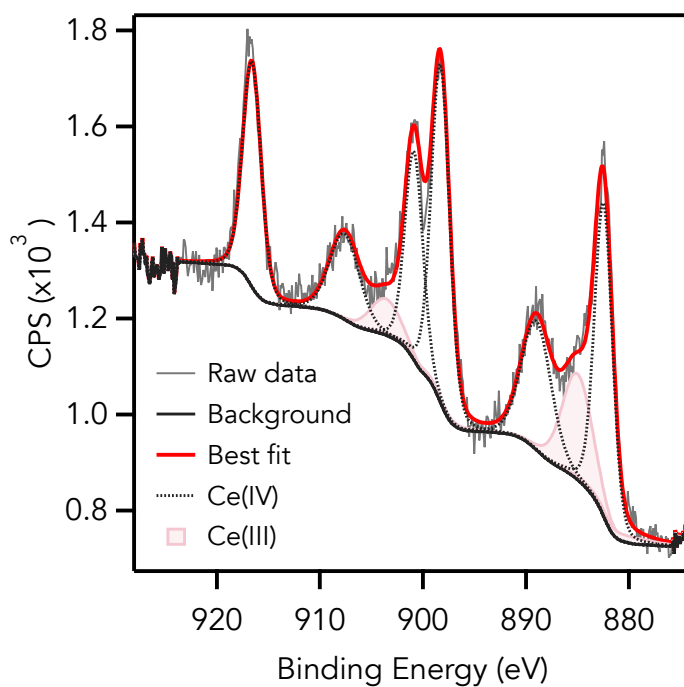


Figure 2.25. High resolution Ce 3d XPS spectrum of as-synthesized In-CeO₂.

Table 2.9. High resolution Ce 3d XPS fitting components of as-synthesized In-CeO₂.

Name	Ce(IV)						Ce(III)			
	v	u	v''	u''	v'''	u'''	v^0	u^0	v'	u'
Position	882.5	900.8	889.0	907.6	898.3	916.6	881.0	899.3	885.0	903.6
FWHM	2.06	2.06	3.41	3.41	2.10	2.10	7.09	7.09	3.51	3.51
Area	1541.83	1027.88	1047.69	698.46	1694.27	1129.51	123.22	82.14	888.97	306.25

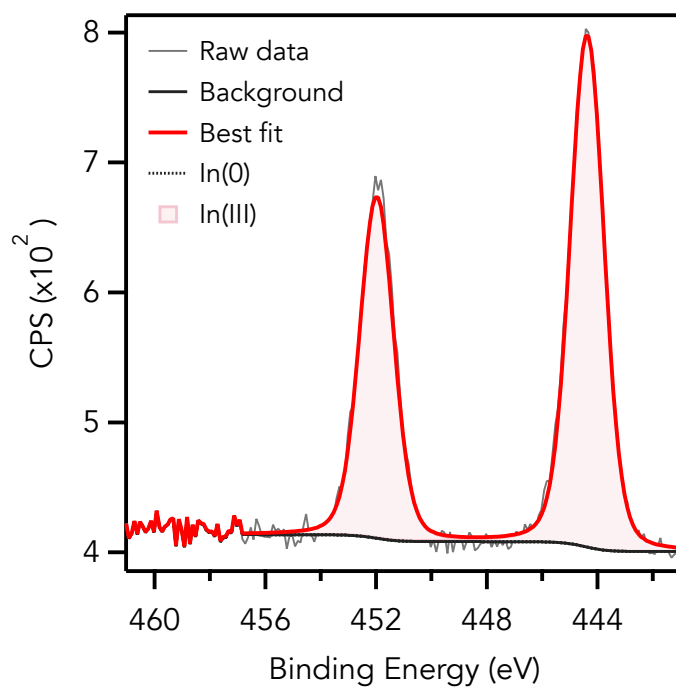


Figure 2.26. High resolution In 3d XPS spectrum of as-synthesized In-CeO₂.

Table 2.10. High resolution In 3d XPS fitting components of as-synthesized In-CeO₂.

Name	In(III), 3d _{5/2}	In(III), 3d _{3/2}	In(0), 3d _{5/2}	In(0), 3d _{3/2}
Position	444.4	452.0	443.5	451.1
FWHM	1.44	1.44	9.68	9.68
Area	651.91	434.60	0.00	0.00

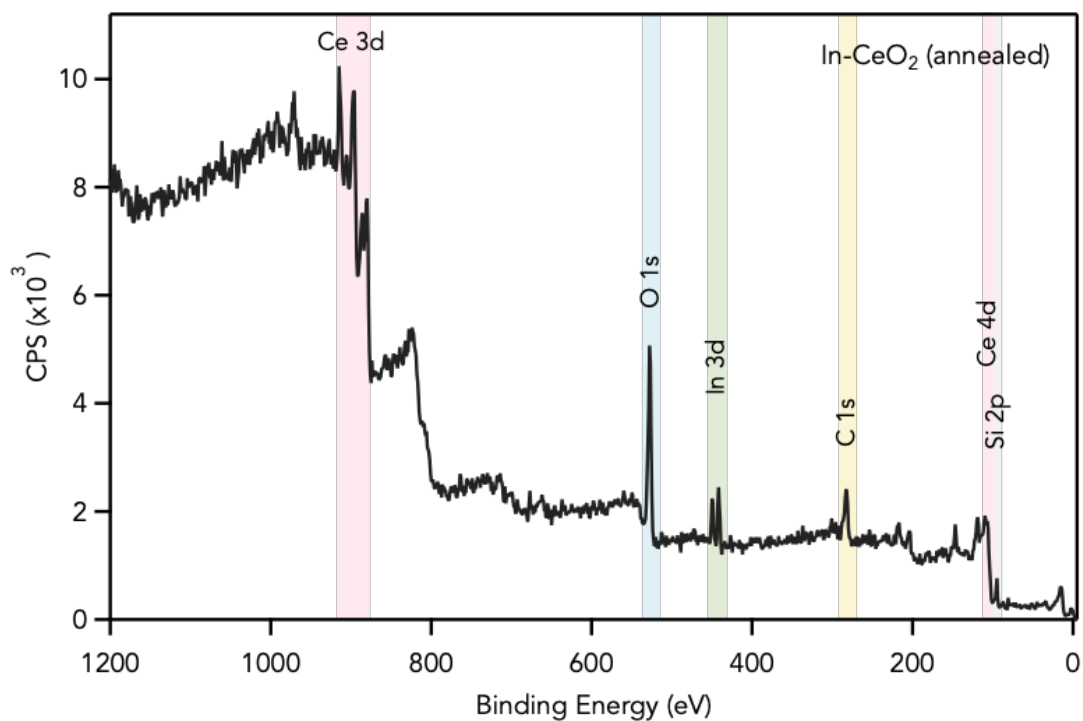


Figure 2.27. XPS survey spectrum of annealed In-CeO₂.

Table 2.11. XPS survey spectrum composition table of annealed In-CeO₂.

Peak	Type	Binding Energy (eV)	Atomic %
Ce	3d	896	15.3
O	1s	528	41.2
In	3d	442	1.4
C	1s	283	36.1
Si	2p	95	5.9

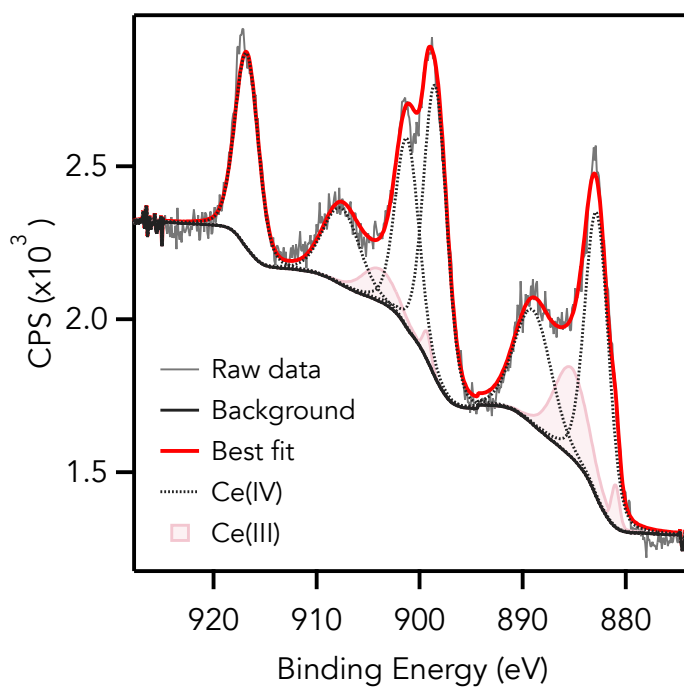


Figure 2.28. High resolution Ce 3d XPS spectrum of annealed In-CeO₂.

Table 2.12. High resolution Ce 3d XPS fitting components of annealed In-CeO₂.

Name	Ce(IV)						Ce(III)			
	ν	u	ν''	u''	ν'''	u'''	ν^0	u^0	ν'	u'
Position	882.8	901.2	889.0	907.6	898.5	916.8	881.0	899.3	885.3	903.9
FWHM	2.70	2.70	4.17	4.17	2.65	2.65	0.92	0.92	3.92	3.92
Area	2885.68	1923.79	1791.29	1194.19	2903.37	1935.58	147.40	98.27	1317.45	483.29

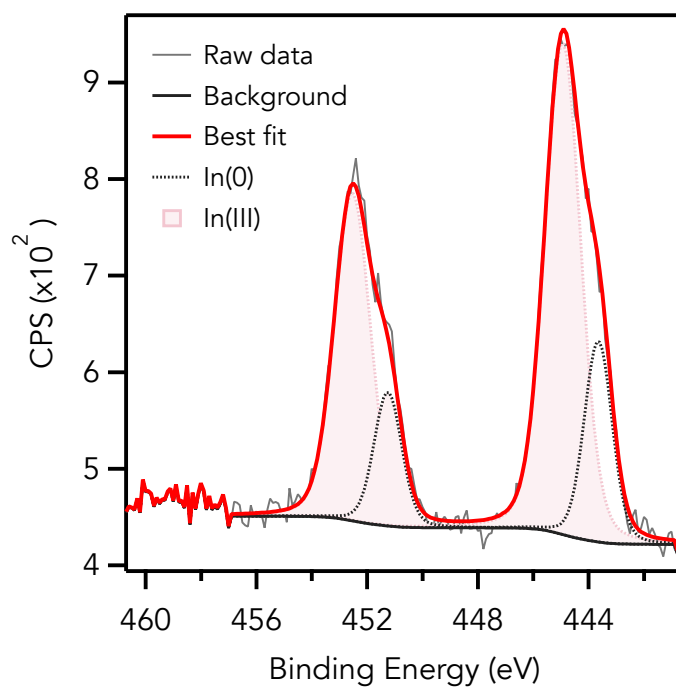


Figure 2.29. High resolution In 3d XPS spectrum of annealed In-CeO₂.

Table 2.13. High resolution In 3d XPS fitting components of annealed In-CeO₂.

Name	In(III), 3d _{5/2}	In(III), 3d _{3/2}	In(0), 3d _{5/2}	In(0), 3d _{3/2}
Position	444.9	452.5	443.7	451.3
FWHM	1.54	1.54	1.19	1.19
Area	898.90	599.27	283.58	189.05

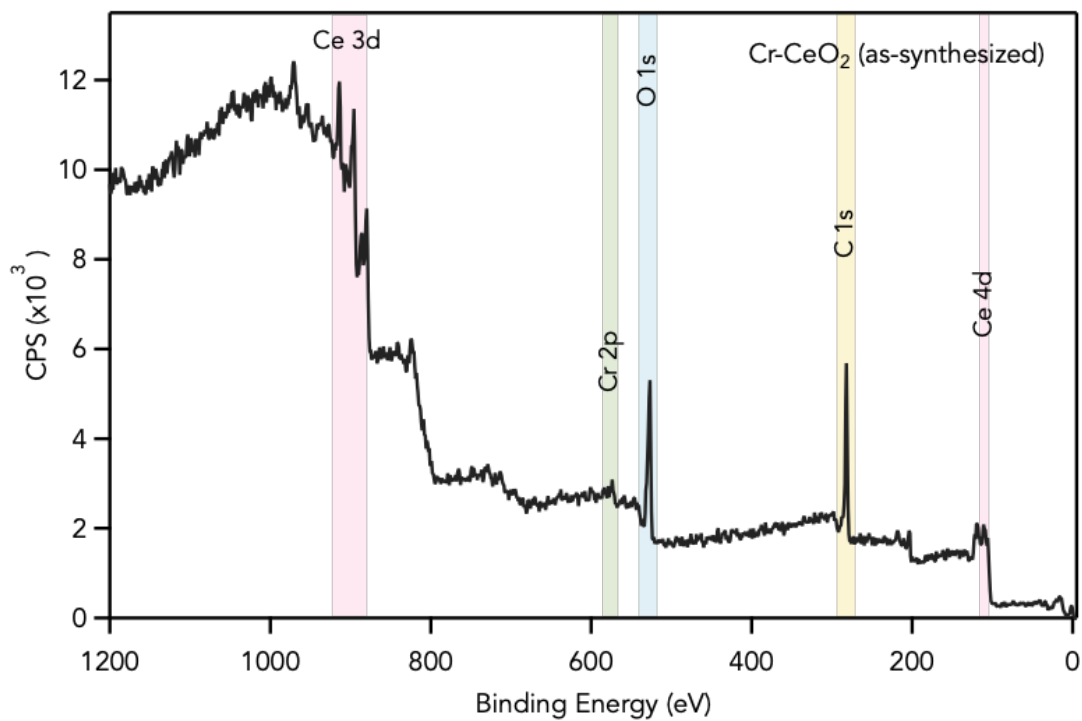


Figure 2.30. XPS survey spectrum of as-synthesized Cr-CeO₂.

Table 2.14. XPS survey spectrum composition table of as-synthesized Cr-CeO₂.

Peak	Type	Binding Energy (eV)	Atomic %
Ce	3d	896	9.0
O	1s	527	27.1
C	1s	282	62.0
Cr	2p	574	1.9

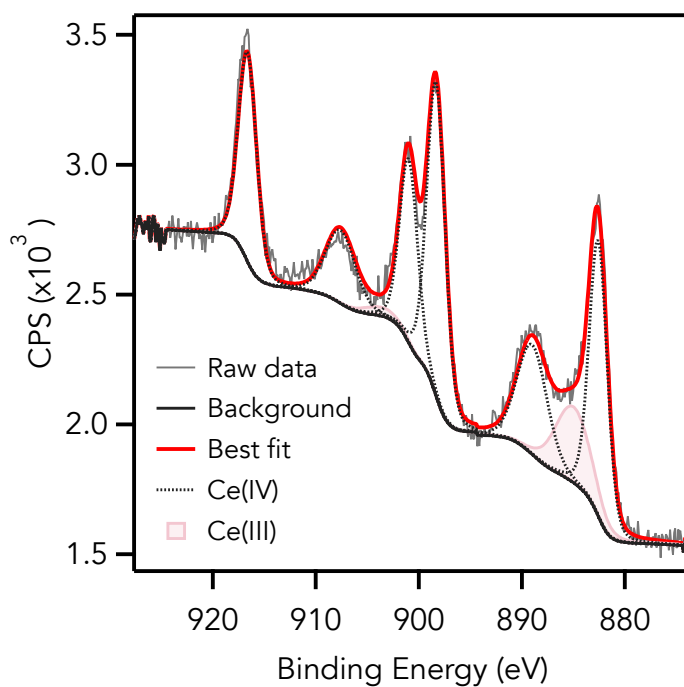


Figure 2.31. High resolution Ce 3d XPS spectrum of as-synthesized Cr-CeO₂.

Table 2.15. High resolution Ce 3d XPS fitting components of as-synthesized Cr-CeO₂.

Name	Ce(IV)						Ce(III)			
	v	u	v''	u''	v'''	u'''	v^0	u^0	v'	u'
Position	882.6	901.0	889.0	907.6	898.3	916.6	880.0	898.3	885.0	903.6
FWHM	2.08	2.08	3.44	3.44	2.09	2.09	14.50	14.50	4.06	4.06
Area	2525.79	1683.86	1665.33	1110.22	2895.69	1930.46	101.13	67.42	1359.27	160.17

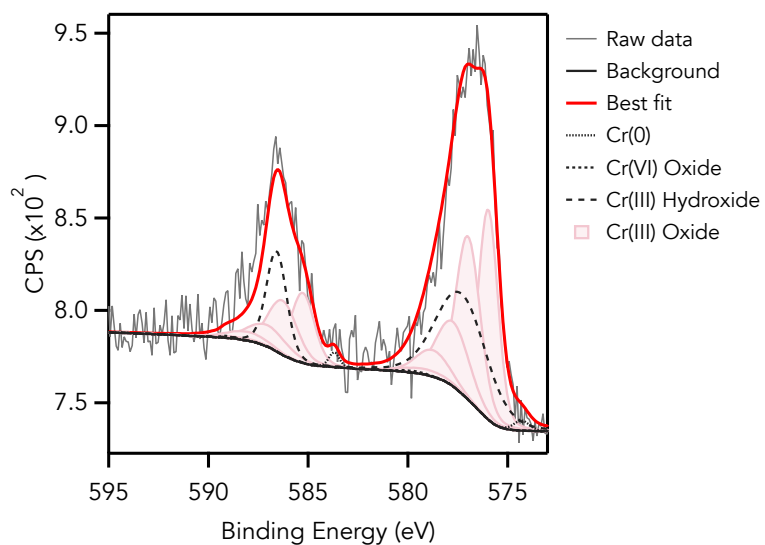


Figure 2.32. High resolution Cr 2p XPS spectrum of as-synthesized Cr-CeO₂.

Table 2.16. High resolution Cr 2p XPS fitting components of as-synthesized Cr-CeO₂.

Name	Cr(0)	3Cr(III) Oxide					Cr(III) Hydroxide	Cr(VI) Oxide
	2p _{3/2}	Peak 1 _{3/2}	Peak 2 _{3/2}	Peak 3 _{3/2}	Peak 4 _{3/2}	Peak 5 _{3/2}	2p _{3/2}	2p _{3/2}
Position	574.3	576.0	577.0	577.8	578.8	579.2	577.3	579.8
FWHM	0.92	1.15	1.43	1.94	2.00	3.00	3.02	1.50
Area	5.70	149.79	145.30	77.89	32.95	10.43	186.67	1.72
Name	2p _{1/2}	Peak 1 _{1/2}	Peak 2 _{1/2}	Peak 3 _{1/2}	Peak 4 _{1/2}	Peak 5 _{1/2}	2p _{1/2}	2p _{1/2}
Position	583.7	585.3	586.3	587.1	588.1	588.5	586.6	589.1
FWHM	0.62	1.38	1.72	2.33	2.40	3.60	1.20	0.51
Area	5.70	59.92	58.12	31.16	13.18	4.17	74.67	0.69

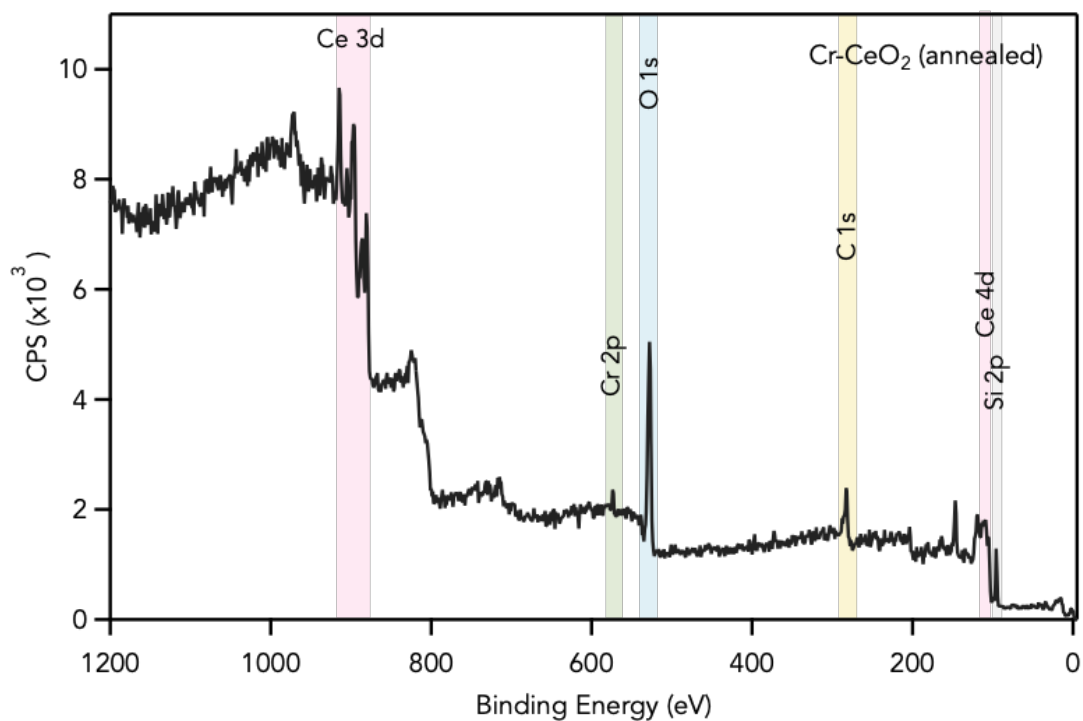


Figure 2.33. XPS survey spectrum of annealed Cr-CeO₂.

Table 2.17. XPS survey spectrum composition table of annealed Cr-CeO₂.

Peak	Type	Binding Energy (eV)	Atomic %
Ce	3d	896	11.7
O	1s	528	44.5
C	1s	283	30.2
Cr	2p	574	2.7
Si	2p	96	10.8

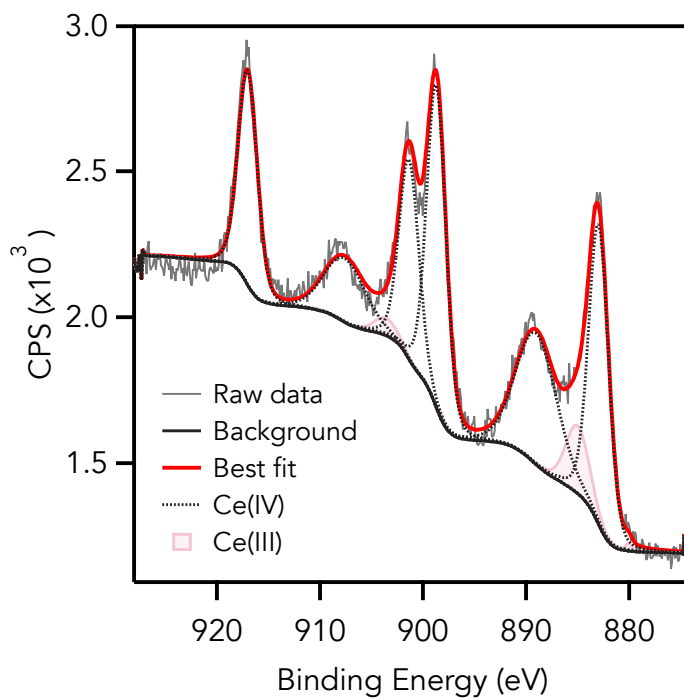


Figure 2.34. High resolution Ce 3d XPS spectrum of annealed Cr-CeO₂.

Table 2.18. High resolution Ce 3d XPS fitting components of annealed Cr-CeO₂.

Name	Ce(IV)						Ce(III)			
	ν	u	ν''	u''	ν'''	u'''	ν^0	u^0	ν'	u'
Position	883.0	901.4	889.0	907.6	898.7	917.0	880.1	898.4	885.0	903.6
FWHM	2.28	2.28	4.65	4.65	2.19	2.19	0.77	0.77	2.68	2.68
Area	2682.31	1788.21	2398.83	1167.18	2776.29	1850.86	21.21	14.14	715.81	183.10

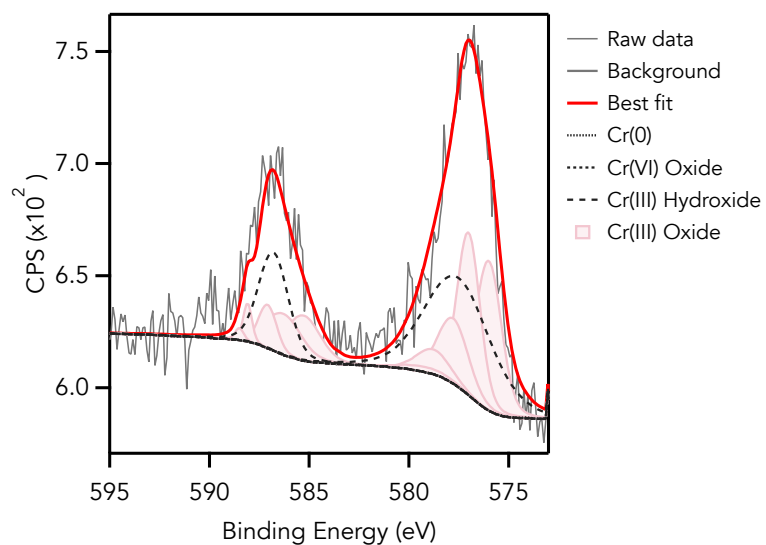


Figure 2.35. High resolution Cr 2p XPS spectrum of annealed Cr-CeO₂.

Table 2.19. High resolution Cr 2p XPS fitting components of annealed Cr-CeO₂.

Name	Cr(0)	3Cr(III) Oxide					Cr(III) Hydroxide	Cr(VI) Oxide
	2p _{3/2}	Peak 1 _{3/2}	Peak 2 _{3/2}	Peak 3 _{3/2}	Peak 4 _{3/2}	Peak 5 _{3/2}	2p _{3/2}	2p _{3/2}
Position	574.1	576.0	577.0	577.8	578.8	579.2	577.5	579.5
FWHM	0.52	1.51	1.35	1.80	2.00	3.00	3.96	0.51
Area	0.22	115.53	112.06	60.07	25.42	8.04	221.06	0.00
Name	2p _{1/2}	Peak 1 _{1/2}	Peak 2 _{1/2}	Peak 3 _{1/2}	Peak 4 _{1/2}	Peak 5 _{1/2}	2p _{1/2}	2p _{1/2}
Position	583.5	586.8	588.8	586.8	588.8	586.8	586.8	588.8
FWHM	0.35	1.76	8.88	1.76	8.88	1.76	1.76	8.88
Area	0.22	88.42	0.00	88.42	0.00	88.42	88.42	0.00

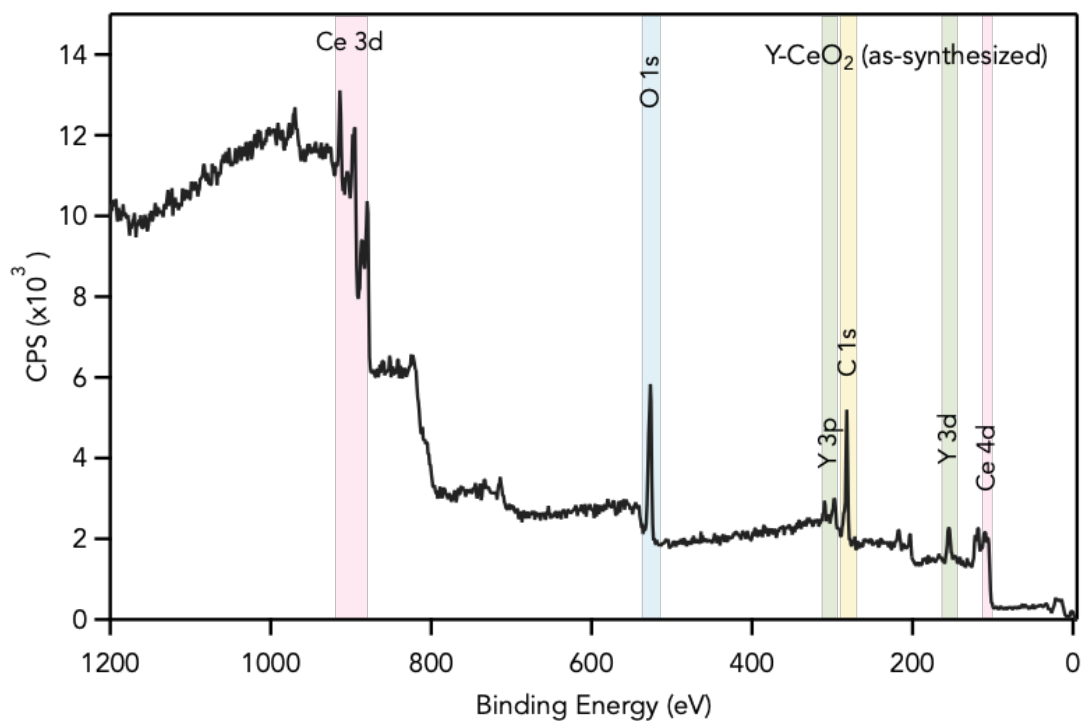


Figure 2.36. XPS survey spectrum of as-synthesized Y-CeO₂.

Table 2.20. XPS survey spectrum composition table of as-synthesized Y-CeO₂.

Peak	Type	Binding Energy (eV)	Atomic %
Ce	3d	895	11.0
O	1s	527	32.4
C	1s	282	52.3
Y	3p	298	4.4
Si	2p	Detected	

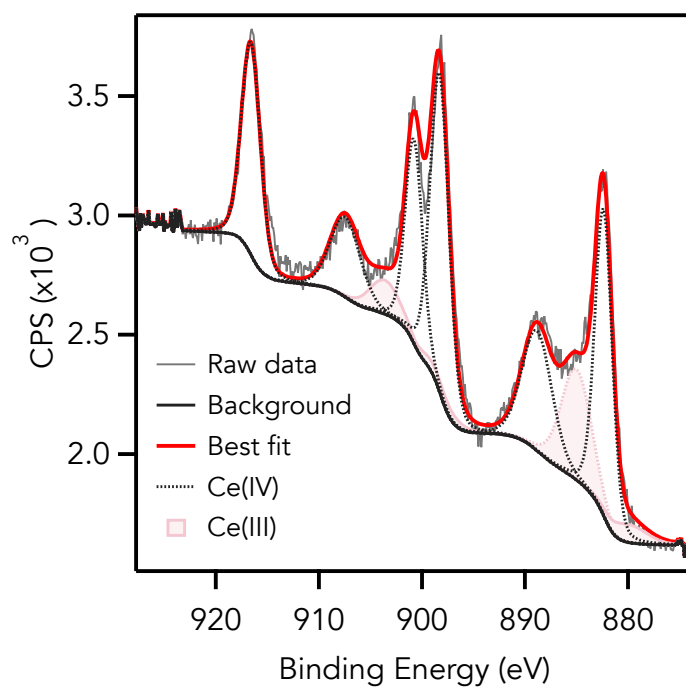


Figure 2.37. High resolution Ce 3d XPS spectrum of as-synthesized Y-CeO₂.

Table 2.21. High resolution Ce 3d XPS fitting components of as-synthesized Y-CeO₂.

Name	Ce(IV)						Ce(III)			
	ν	u	ν''	u''	ν'''	u'''	ν^0	u^0	ν'	u'
Position	882.4	900.8	888.8	907.4	898.3	916.6	880.0	898.3	885.0	903.6
FWHM	1.98	1.98	3.43	3.43	2.16	2.16	4.27	4.27	3.49	3.49
Area	2913.87	1942.58	1976.59	1317.72	3300.59	2200.39	370.57	247.05	1858.25	570.39

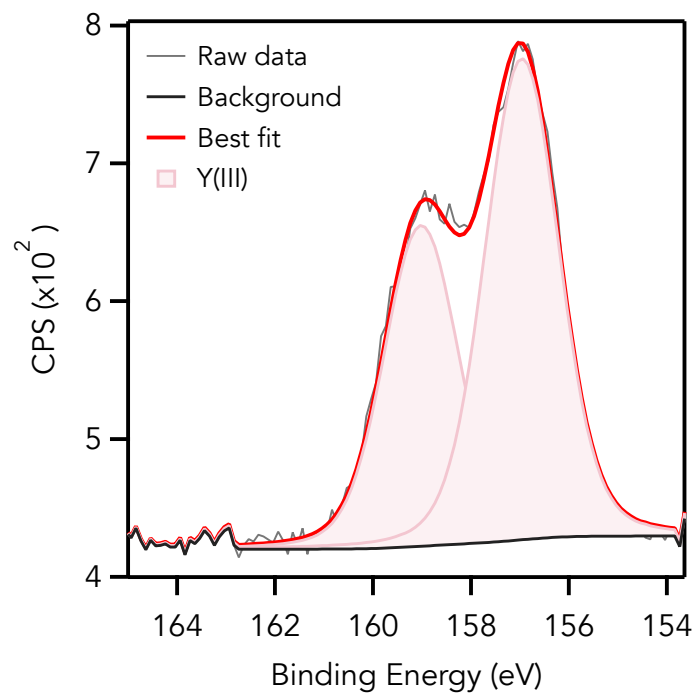


Figure 2.38. High resolution Y 3d XPS spectrum of as-synthesized Y-CeO₂.

Table 2.22. High resolution Y 3d XPS fitting components of as-synthesized Y-CeO₂.

Name	Y(III), 3d _{5/2}	Y(III), 3d _{3/2}
Position	157.0	159.0
FWHM	1.78	1.78
Area	712.28	474.85

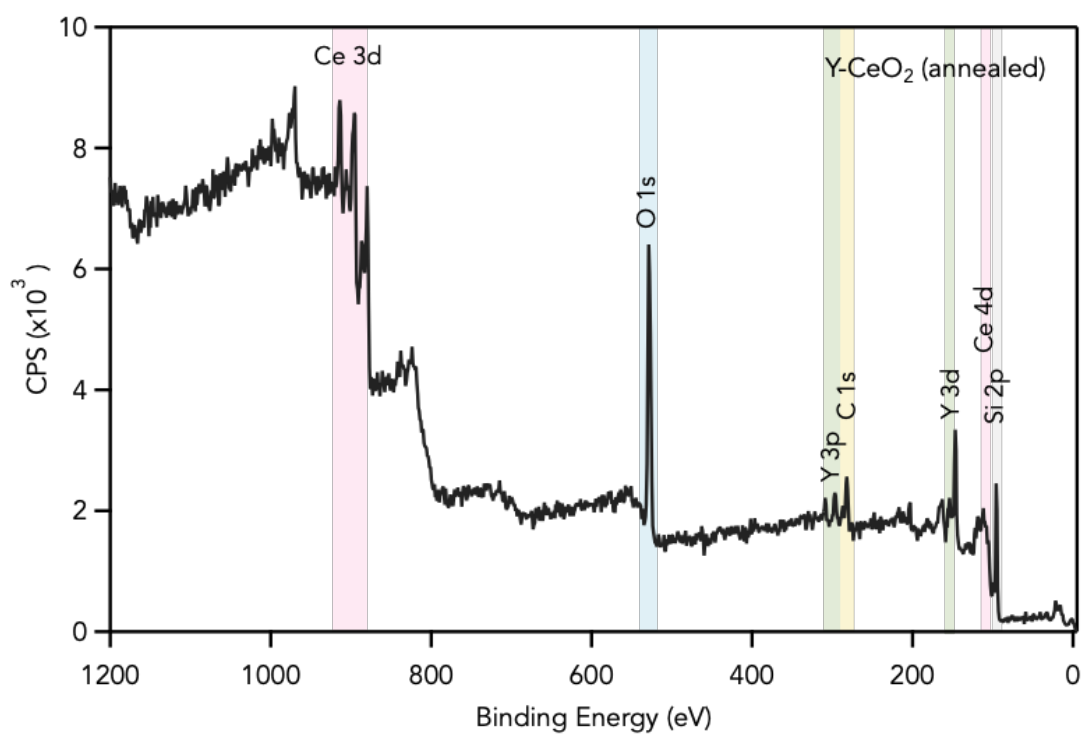


Figure 2.39. XPS survey spectrum of annealed Y-CeO₂.

Table 2.23. XPS survey spectrum composition table of annealed Y-CeO₂.

Peak	Type	Binding Energy (eV)	Atomic %
Ce	3d	895	11.4
O	1s	527	43.2
C	1s	282	19.1
Y	3p	297	2.1
Si	2p	96	24.2

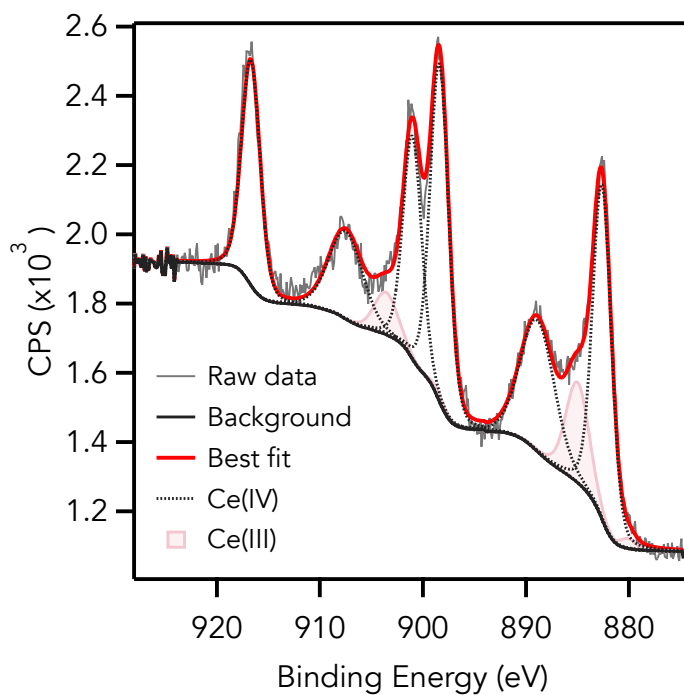


Figure 2.40. High resolution Ce 3d XPS spectrum of annealed Y-CeO₂.

Table 2.24. High resolution Ce 3d XPS fitting components of annealed Y-CeO₂.

Name	Ce(IV)						Ce(III)			
	ν	u	ν''	u''	ν'''	u'''	ν^0	u^0	ν'	u'
Position	882.6	901.0	888.9	907.5	898.4	916.7	880.1	898.4	885.0	903.6
FWHM	2.14	2.14	3.90	3.90	2.12	2.12	1.78	1.78	2.65	2.65
Area	2371.32	1580.88	1697.33	1131.55	2367.63	1578.42	59.42	39.61	881.39	371.64

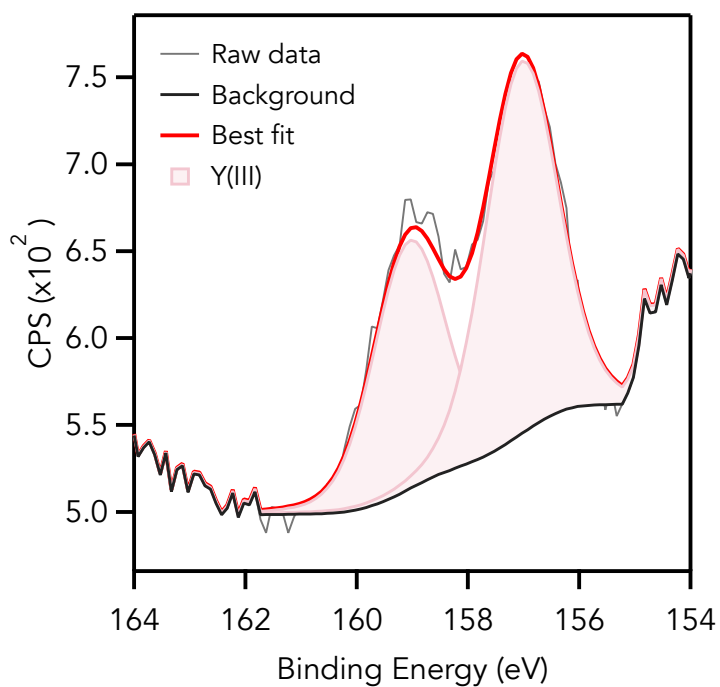


Figure 2.41. High resolution Y 3d XPS spectrum of annealed Y-CeO₂.

Table 2.25. High resolution Y 3d XPS fitting components of annealed Y-CeO₂.

Name	Y(III), 3d5/2	Y(III), 3d3/2
Position	157.0	159.1
FWHM	1.54	1.54
Area	377.16	251.44

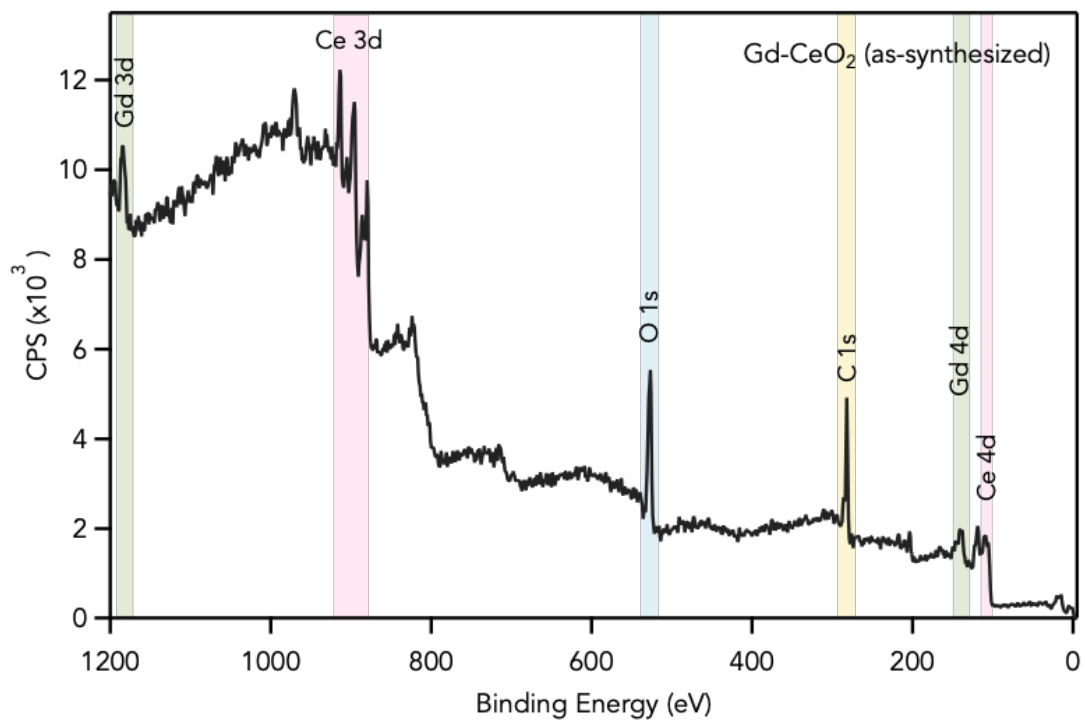


Figure 2.42. XPS survey spectrum of as-synthesized Gd-CeO₂.

Table 2.26. XPS survey spectrum composition table of as-synthesized Gd-CeO₂.

Peak	Type	Binding Energy (eV)	Atomic %
Ce	3d	895	10.4
O	1s	527	34.5
C	1s	282	52.5
Gd	4d	138	2.6

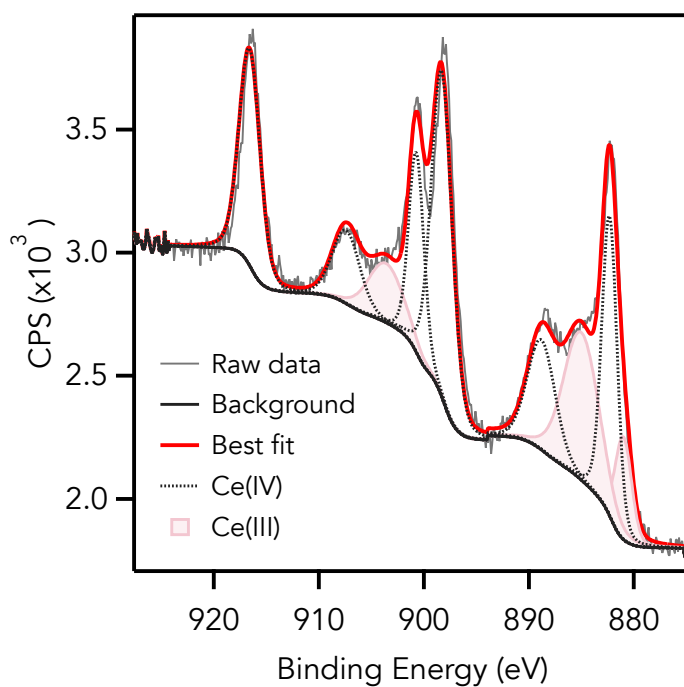


Figure 2.43. High resolution Ce 3d XPS spectrum of as-synthesized Gd-CeO₂.

Table 2.27. High resolution Ce 3d XPS fitting components of as-synthesized Gd-CeO₂.

Name	Ce(IV)						Ce(III)			
	ν	u	ν''	u''	ν'''	u'''	ν^0	u^0	ν'	u'
Position	882.3	900.7	888.8	907.4	898.3	916.6	881.0	899.3	885.0	903.6
FWHM	1.72	1.72	3.11	3.11	2.35	2.35	1.85	1.85	4.00	4.00
Area	2398.22	1598.85	1590.25	1060.17	3562.31	2374.87	884.79	0.00	2747.16	1102.63

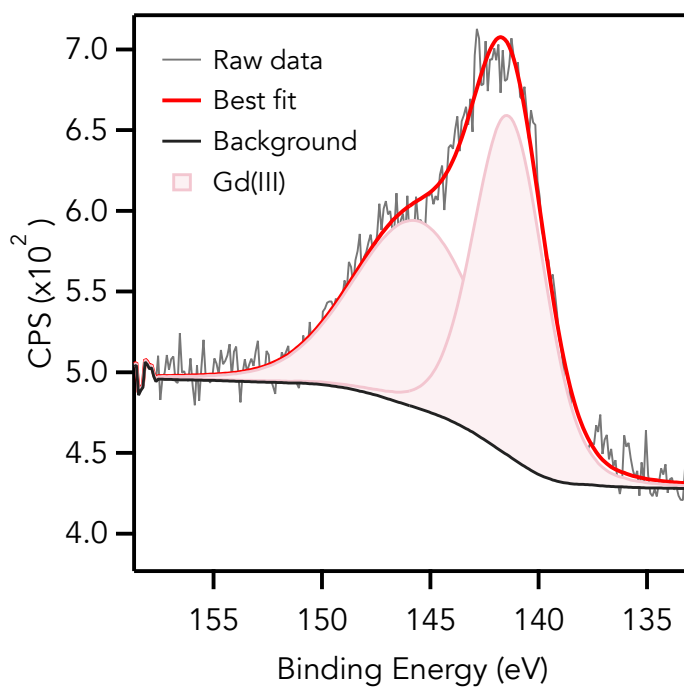


Figure 2.44. High resolution Gd 4d XPS spectrum of annealed Gd-CeO₂.

Table 2.28. High resolution Gd 4d XPS fitting components of annealed Gd-CeO₂.

Name	Gd(III), 4d _{5/2}	Gd(III), 4d _{3/2}
Position	141.4	145.5
FWHM	3.83	6.93
Area	924.37	920.80

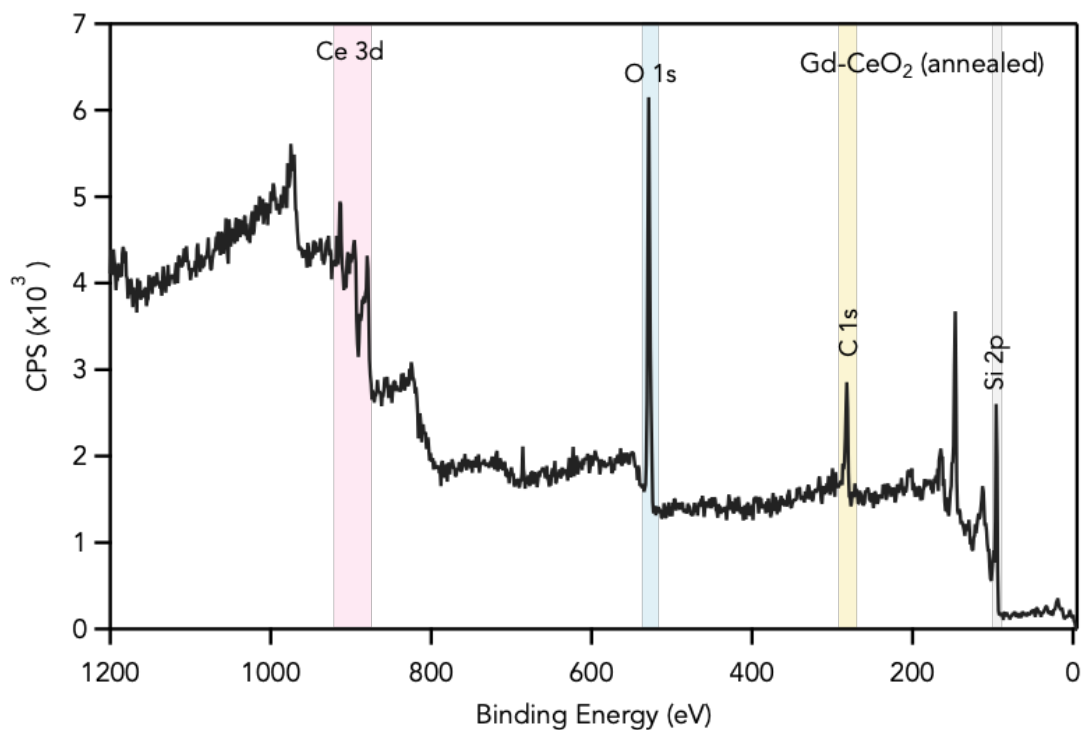


Figure 2.45. XPS survey spectrum of annealed Gd-CeO₂.

Table 2.29. XPS survey spectrum composition table of annealed Gd-CeO₂. *Gd was not detected for this sample due to sample quality, but ICP-OES confirms Gd is 15.8% before catalysis and 16.3% after catalysis.

Peak	Type	Binding Energy (eV)	Atomic %
Ce	3d	880	25.92
O	1s	529	24.87
F	1s	686	0.53
C	1s	282	17.96
Si	2p	96	30.71
Gd	Not detected*		

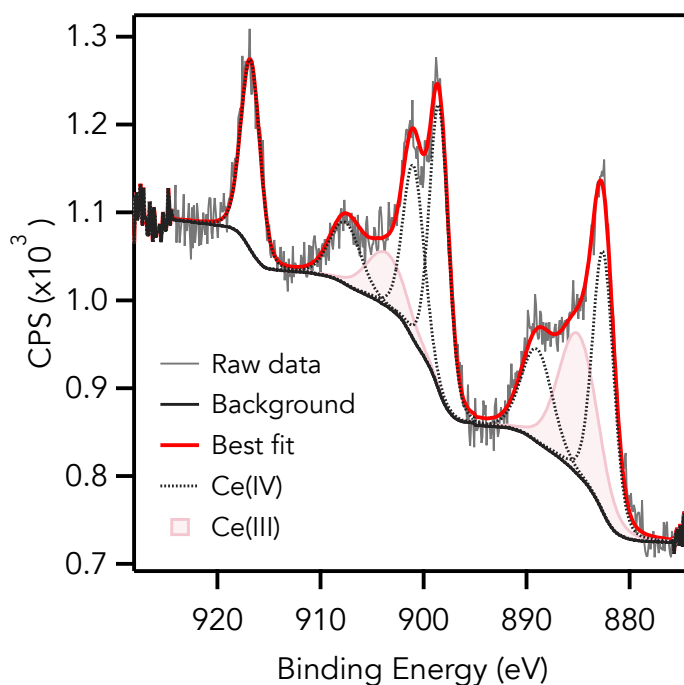


Figure 2.46. High resolution Ce 3d XPS spectrum of annealed Gd-CeO₂.

Table 2.30. High resolution Ce 3d XPS fitting components of annealed Gd-CeO₂.

Name	Ce(IV)						Ce(III)			
	ν	u	ν''	u''	ν'''	u'''	ν^0	u^0	ν'	u'
Position	882.6	901.0	889.0	907.6	898.5	916.8	880.2	898.5	885.0	903.6
FWHM	2.41	2.41	3.54	3.54	2.18	2.18	20.07	20.07	4.46	4.46
Area	820.17	546.78	428.74	285.83	810.88	540.59	0.00	0.00	821.82	311.95

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Chapter 3.

Optically Active Yb³⁺ Spin Defects in Cerium Oxide Nanocrystals

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3.1 Introduction

Quantum information technology is gaining significant momentum because of its promise to transform sensing,^{1,2,3} communications,^{4,5} and computing.^{6,7,8,9} Among the wide variety of potential qubit candidates, optically addressable spin defects in crystalline hosts are of particular interest due to their flexibility as robust qubits for scalable quantum systems.^{10,11,12} Nanoscale material platforms offer a high degree of control over facets, morphologies, surface-to-volume ratios, local electromagnetic environments, and processability. Atom-level tunability of both the core and surface, enabled by solution-phase chemistry, offers a unique approach to mitigating environmental decoherence while still allowing proximity to promote quantum sensing and integration into photonic platforms for optical addressability.^{12,13} However, nanoscale systems also exacerbate issues that are less severe in bulk crystals, such as a higher ratio of surface defects, proximity to those surfaces, or proximity to exogenous nuclear spins, all of which impact decoherence.^{14,15}

Recent studies have demonstrated the potential of rare earth ions doped into inorganic solids for quantum information science, owing to their excellent photoluminescence properties and spin coherence for spin-optical interfaces.^{9,16,17,18,19,20} Additionally, seminal studies on ensembles of lanthanide-doped nanocrystals and single crystals have demonstrated upconversion and single photon emission.^{21,22,23} Cerium oxide has attracted interest as a qubit host lattice due to its near-zero natural abundance of nuclear spins (Ce

has no magnetic isotopes, and ^{17}O has a natural abundance of 0.037–0.040%).^{10,16,24,25} Other requirements of an ideal qubit host lattice include low nuclear gyromagnetic ratios, the ability to control and mitigate crystal growth defects, and spatial separation of non-zero nuclear spin isotopes to prevent decoherence.¹⁰ In principle, stoichiometric CeO_2 offers a non-magnetic electron-spin-free lattice since Ce^{4+} is diamagnetic. However, it is well known that nanocrystalline CeO_2 is often nonstoichiometric (CeO_{2-x}), resulting in significant concentrations of paramagnetic Ce^{3+} due to its high tolerance to oxygen vacancy defects and the ease of reversible conversion of Ce^{4+} to Ce^{3+} .^{26,27,28,29}

Several studies of CeO_2 nanocrystals have aimed to understand how to control size, morphology, and concentrations of defects and dopants.²⁹ In the realm of catalysis, doped CeO_2 has long been studied to generate unique active-site environments by exploiting both the dopant properties and the balance of Ce^{4+} , Ce^{3+} , and oxygen vacancies.^{30,31,32} In the context of quantum technology, CeO_2 has only recently been investigated as a host lattice for lanthanide ions as spin qubits in both thin films and nanocrystals. Multiple studies of Er^{3+} -doped CeO_2 (via single crystalline thin films and nanocrystal ensembles) have demonstrated millisecond-long spin lifetimes and near microsecond-long coherence times at 3.2 K, experimentally supporting the promise of CeO_2 as a host lattice.^{9,16,33,34} However, the negative impact of surface and defect-related decoherence was identified as a significant challenge, prompting the need for further study and synthetic development. In pursuit of this goal, we investigated cerium oxide as a host for optically active Yb^{3+} spin qubits. Yb^{3+} was chosen because of its relatively simple electronic structure and its strong spectroscopic signature in the near-infrared. Previous studies on Yb^{3+} -doped CeO_2 have focused on its use as a catalyst in solid oxide fuel cells and electrolyzers,^{35,36} as a medium for identifying the hyperfine structure and luminescent properties of Yb^{3+} ,^{37,38,39,40,41} and applications in quantum cutting and upconversion nanomaterials.^{42,43,44,45,46}

This work turns a unique lens on Yb^{3+} as an optically active spin qubit with an in-depth critique of CeO_2 as a host for Yb^{3+} emissive and spin properties, which, to our knowledge, has not yet been reported. Varying the Yb^{3+} concentration, we characterize the dopant's optical response at room temperature and 4 K and demonstrate that annealing the nanocrystals at 700 °C significantly improves the excited-state lifetimes.

Finally, we quantify the spin coherence via EPR spectroscopy and demonstrate that annealing the nanocrystals also improves the T_1 lifetime.

3.2 Results and Discussion

3.2.1 Synthesis and Photoluminescence of Yb^{3+} -Doped CeO_2 Nanocrystals

Yb^{3+} -doped CeO_2 ($\text{CeO}_2:\text{Yb}^{3+}$) was synthesized by thermal decomposition of cerium(III) nitrate ($1-x$ eq.), ytterbium(III) nitrate ($x = 0.001, 0.005, 0.01, 0.05$, and 0.1 eq.), and oleylamine (3 eq.) in a bath of 1-octadecene, adapted from a previously reported method.⁴⁷ The resulting oleylamine-capped nanocrystals were colloidally stable in nonpolar solvents and characterized via transmission electron microscopy (TEM) and powder X-ray diffraction (PXRD), as shown in **Figure 3.1**. Yb^{3+} concentrations within the CeO_2 nanocrystals were measured by inductively coupled plasma–optical emission spectroscopy (ICP-OES) and are reported in **Figure 3.1** for the corresponding nanocrystal samples, showing that Yb^{3+} is incorporated close to the intended doping percentage (0.1, 0.5, 1, 5, and 10 percent, respectively). High-resolution TEM (HR-TEM) images revealed spherical, highly crystalline particles with lattice fringes assigned to the (111) plane of the fluorite lattice (**Figure 3.2**). A comparison of the size distributions measured by manual TEM image analysis to the Scherrer analysis of the XRD using pseudo-Voigt fits indicated a small discrepancy between the observed nanocrystal diameters and nanocrystalline domain sizes for each $\text{CeO}_2:\text{Yb}^{3+}$ sample (**Figure 3.3** for PXRD peak fittings).⁴⁸ For example, the **0.08% Yb** sample appears to have an average measured diameter of 8.8 ± 1.1 nm by TEM but an average crystalline domain size of 7.0 ± 0.1 nm via Scherrer analysis. On average, the crystalline domain size is ~ 1.3 nm smaller than the measured nanocrystal size by TEM. This result suggests that the as-synthesized nanocrystals may have a defect-rich surface layer of Ce^{3+} and oxygen vacancies that reduce the overall crystalline domain. Prior literature has demonstrated that the (111) surface plane is prone to a reduced Ce^{3+} shell with an average thickness of ~ 0.8 nm, which may account for the discrepancy in TEM and XRD sizes.⁴⁹

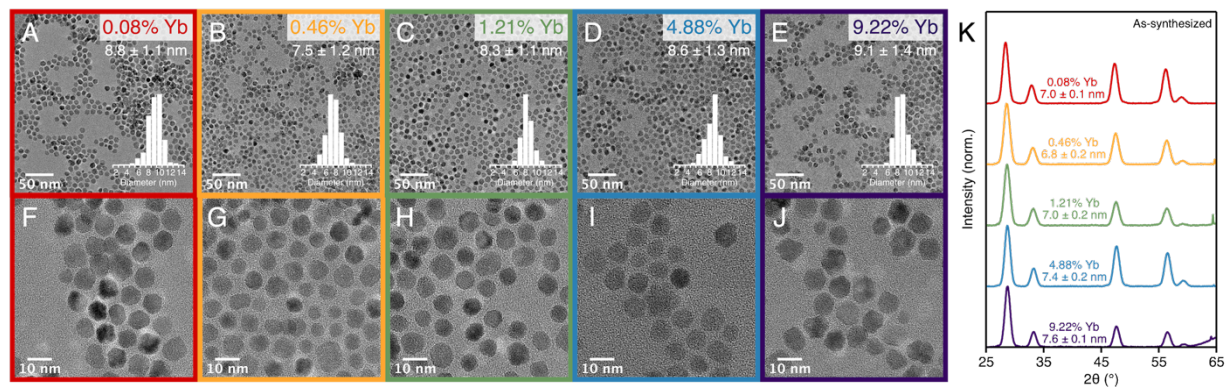


Figure 3.1. (A-E) TEM, (F-J) HR-TEM, and (K) PXRD of as-synthesized $\text{CeO}_2\text{:Yb}^{3+}$ nanocrystals.

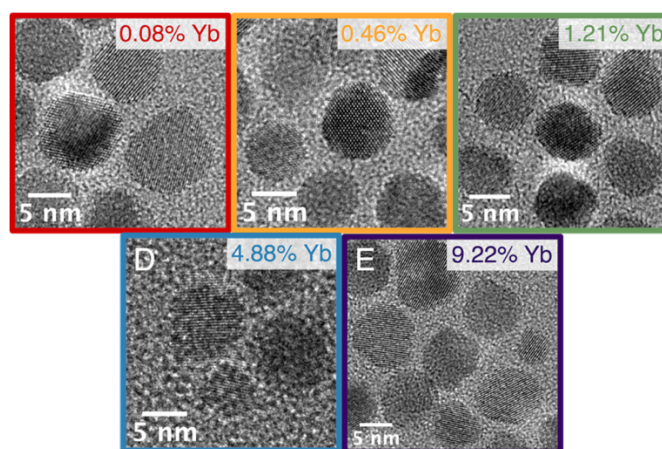


Figure 3.2. High resolution TEM of as-synthesized Yb^{3+} -doped CeO_2 showing lattice fringes.

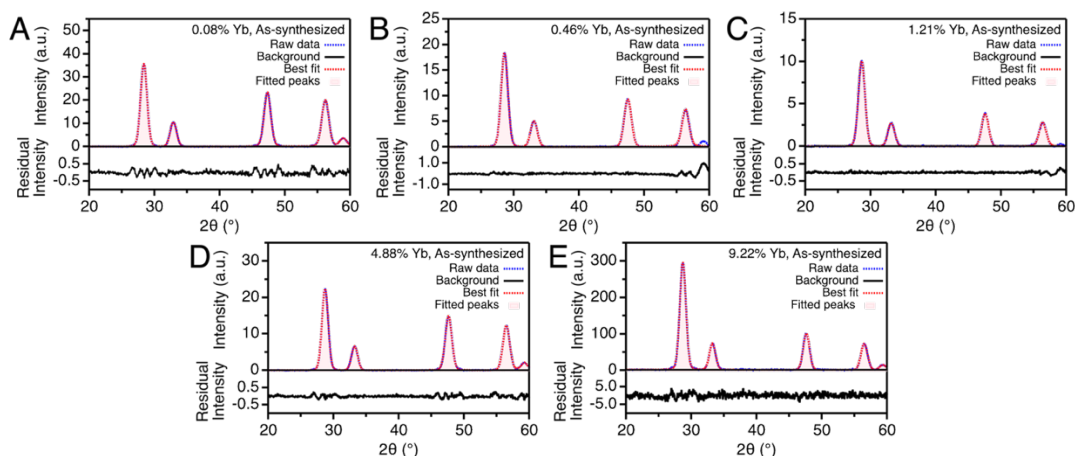


Figure 3.3. Multippeak pseudo-Voigt fits and residual fits for PXRD data of (A) 0.08%, (B) 0.46%, (C) 1.21%, (D) 4.88%, and (E) 9.22% as-synthesized Yb^{3+} -doped CeO_2 .

We first investigated the optical properties of the as-synthesized nanocrystals as a function of Yb^{3+} concentration. We initially probed the CeO_2 -sensitized excitation of Yb^{3+} at 300 K using a broadband xenon arc lamp set at 320 nm (**Figure 3.4**), which falls at the tail end of the broad absorption band peaking at ~ 290 nm observed in the UV-vis absorption spectra. This band corresponds to the charge-transfer transition originating from the CeO_2 O^{2-} $2p$ valence band to Ce^{4+} $4f$ orbitals (**Figure 3.5**).³⁹ Upon 320 nm excitation, we observed characteristic emission of Yb^{3+} between 960–1100 nm, indicating successful energy transfer from the wide-bandgap CeO_2 (3.3–3.6 eV) to Yb^{3+} .^{50,51,52} Signal-to-noise improved with increasing Yb^{3+} concentration, consistent with an increase in energy capture by Yb^{3+} . Time-resolved photoluminescence (TRPL) measurements were collected at 300 K using a μs -pulsed xenon flash lamp and showed poor signal with an initial fast-decay component on the same timescale as the instrument response, as well as a low-intensity slow-decay component, making it difficult to extract accurate lifetimes for comparison. An instrument response function collected under identical conditions confirmed that the initial fast decay is limited by the instrument (**Figure 3.6**). We observed a general trend of lengthening the slow-decay component as the Yb^{3+} concentration decreased from 9.22% Yb to 0.08% Yb.

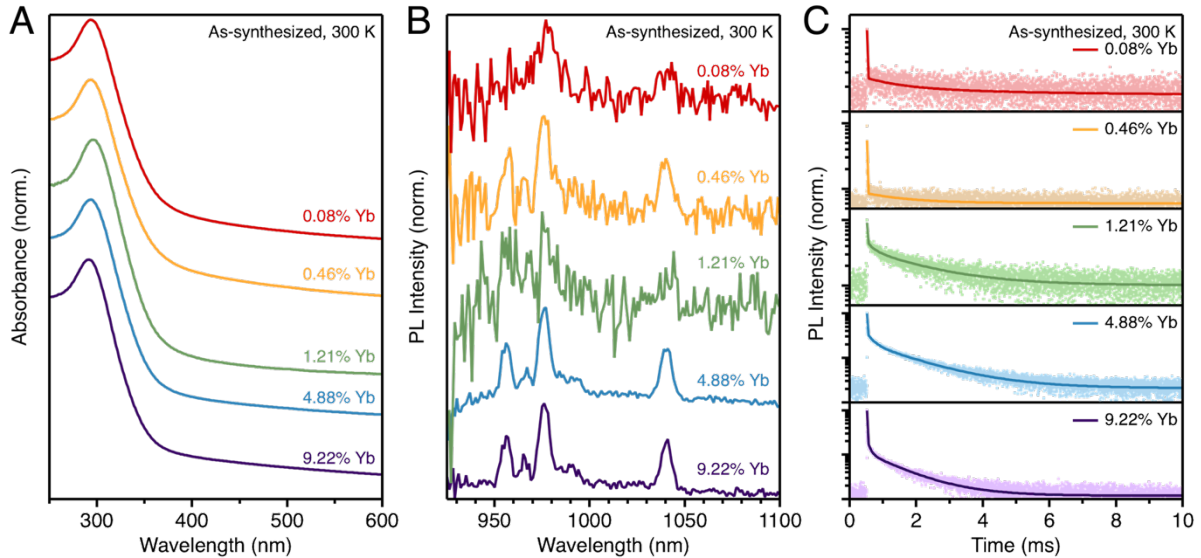


Figure 3.4. (A) UV-vis absorption, (B) PL, and (C) TRPL of as-synthesized Yb^{3+} -doped CeO_2 collected at 300 K via indirect excitation at $\lambda_{\text{ex}} = 320$ nm. TRPL measurements were performed using a xenon μs flash lamp.

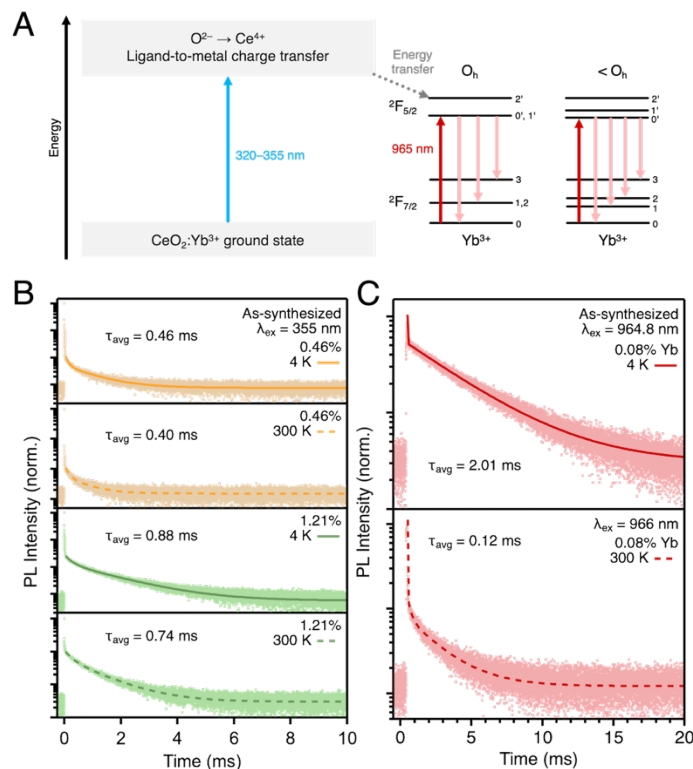


Figure 3.5. (A) Scheme of electronic transitions of Yb^{3+} -doped CeO_2 with arrows showing indirect (blue) and direct (red) excitation and Yb^{3+} emission (light pink). Comparison of Yb^{3+} TRPL by (B) indirect excitation ($\lambda_{\text{ex}} = 355$ nm, $\lambda_{\text{em}} = 1039$ nm) of as-synthesized **0.46% Yb** and **1.21% Yb** at 4 K and 300 K, and (C) direct excitation ($\lambda_{\text{ex}} = 965\text{--}966$ nm, $\lambda_{\text{em}} = 1039$ nm) of **0.08% Yb** at 4 K and 300 K.

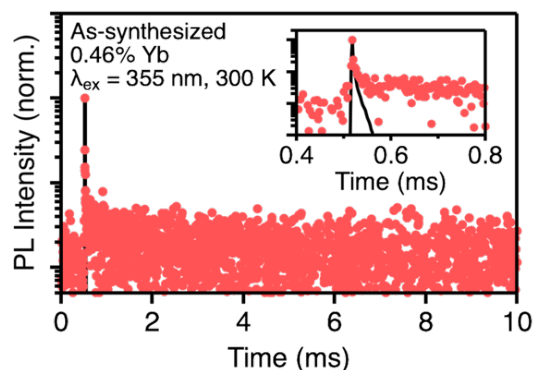


Figure 3.6. TRPL of as-synthesized 0.46% Yb^{3+} -doped CeO_2 (red dots), collected at 300 K using a xenon μs flash lamp. Inset shows the fast decay is IRF-limited. The black data show the instrument response function (IRF).

When we cooled the as-synthesized **0.46% Yb** and **1.21% Yb** samples to 4 K, we observed that the Yb^{3+} emission linewidths narrowed, but broad defect emission became more prominent between 700–1000 nm (**Figure 3.7A,D**). Additionally, we did not observe a significant increase in Yb^{3+} slow-decay component lifetimes nor a decrease in the fast-decay component at 4 K that would indicate freezing out of non-radiative decay pathways (**Figure 3.5B, Table 3.1**). This result suggests that defect states in the as-synthesized nanocrystals remain active even at low temperatures. To mitigate the effects of CeO_2 's native defects on the efficiency of energy transfer to Yb^{3+} , we switched to direct excitation of the Yb^{3+} with a tunable Ti:sapphire laser set to 965 nm (4 K) or 966 nm (300 K) to account for temperature-dependent changes in the Yb^{3+} absorption (**Figure 3.5C, Table 3.2**). We not only observed a reduction of the fast-decay component but also a lengthening of the slower component, which is reflected in an overall increase of the amplitude-weighted average lifetime (τ_{avg}) at both 4 K and 300 K compared to indirect excitation. Nevertheless, a significant fraction of the total Yb^{3+} emission is released with a microsecond lifetime, much faster than the typical radiative decay times of Yb^{3+} (ms), likely indicating the presence of defects in close proximity to Yb^{3+} . To reduce defect density and improve overall crystal quality, we investigated the influence of sample annealing (see the Experimental Methods).

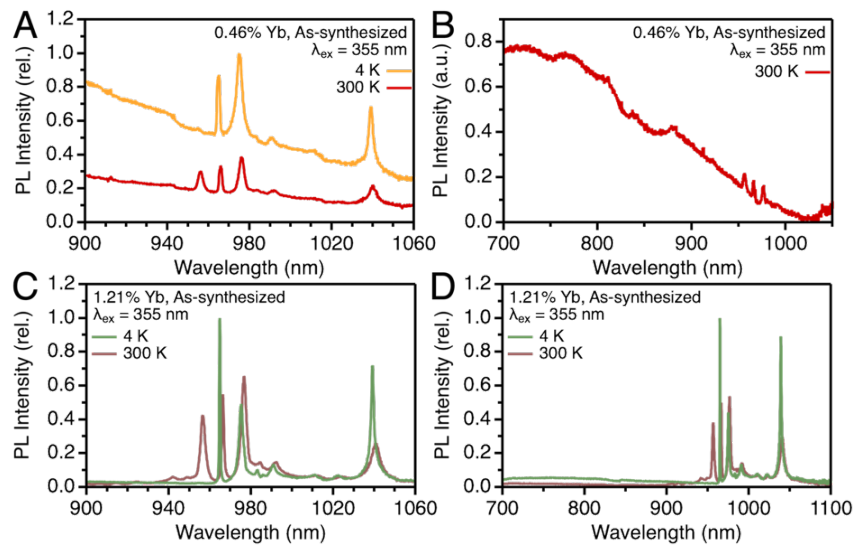


Figure 3.7. PL of as-synthesized Yb^{3+} -doped CeO_2 : (A,B) 0.46% Yb and (C,D) 1.21% Yb at 4 K and 300 K via indirect excitation at $\lambda_{\text{ex}} = 355$ nm.

Table 3.1. Biexponential fits for TRPL of as-synthesized 0.46% and 1.21% Yb³⁺-doped CeO₂ via indirect excitation ($\lambda_{\text{ex}} = 355$ nm, $\lambda_{\text{em}} = 1039$ nm) at 4 K and 300 K.

Sample	A ₁	τ_1 (ms)	A ₂	τ_2 (ms)	τ_{avg} (ms)
0.46% Yb, 4 K	0.006	0.101	0.004	0.996	0.461
0.46% Yb, 300 K	0.005	0.126	0.004	0.713	0.395
1.21% Yb, 4 K	0.012	0.240	0.013	1.517	0.885
1.21% Yb, 300 K	0.044	0.262	0.053	1.133	0.739

Table 3.2. Bi and triexponential fits for TRPL of as-synthesized 0.08% Yb³⁺-doped CeO₂ via direct excitation ($\lambda_{\text{ex}} = 965\text{--}966$ nm, $\lambda_{\text{em}} = 1039$ nm) at 4 K and 300 K.

Sample	A ₁	τ_1 (ms)	A ₂	τ_2 (ms)	A ₃	τ_3 (ms)	τ_{avg} (ms)
0.08% Yb, 4 K	0.521	0.009	0.494	4.114	—	—	2.006
0.08% Yb, 300 K	0.066	2.258	0.062	0.219	1.306	0.004	0.116

As mentioned above, it is well known that cerium oxide is prone to oxygen vacancy defects when aliovalent dopants are introduced into the lattice, yielding non-stoichiometric CeO_{2-x} that is charge-compensated by Ce³⁺ ions.^{26,27,28,29,39} Previous studies have shown that annealing cerium oxide at 500 °C or higher in an oxidizing environment yields larger crystalline domains, reoxidizes Ce³⁺ to Ce⁴⁺, and improves the rare earth's luminescence.^{41,53} Tracking these simple parameters allows us to investigate the extent to which annealing can improve the optical and, importantly, the spin coherence properties. After annealing, TEM and XRD measurements show that the nanocrystalline domain size and nanoparticle size both significantly increased for all concentrations from an average crystalline domain size of ~7 nm to ~20 nm (Figure 3.8A-C, Figure 3.9 for PXRD peak fittings). Visually, the nanocrystal film, which appeared dark brown before annealing due to its high concentration of Ce³⁺ and associated oxygen vacancies (CeO_{2-x}), turned a lighter golden color after annealing.⁵⁴ This color change suggests a decrease in Ce³⁺ and oxygen

vacancies and more stoichiometric CeO₂. We note that the organic oleylamine ligands are burned off at this annealing temperature, leaving bare crystalline surfaces (**Figure 3.10**). We confirmed the decrease of Ce³⁺ by X-ray photoelectron spectroscopy, as shown in **Figure 3.8D-E**, where the high-resolution Ce 3d spectra indicate a smaller Ce³⁺ percentage (shaded area, **Figure 3.11** for peak fitting) after annealing. On average, we observed a decrease in the relative Ce³⁺ content by approximately one-third.

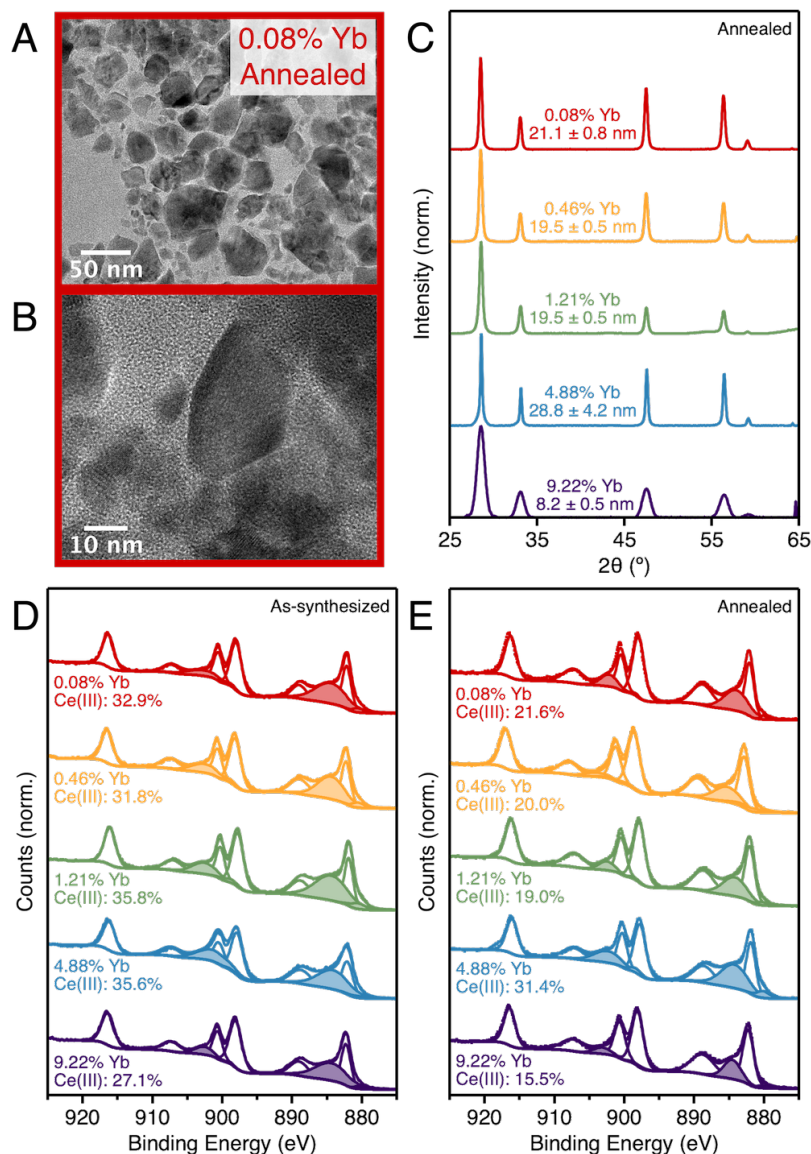


Figure 3.8. Representative (A) TEM and (B) HR-TEM of **0.08% Yb** showing morphology after annealing. (C) PXRD of CeO₂:Yb³⁺ after annealing. High-resolution Ce 3d XPS spectra of CeO₂:Yb³⁺ (D) as-synthesized and (E) after annealing (shaded area indicates Ce³⁺).

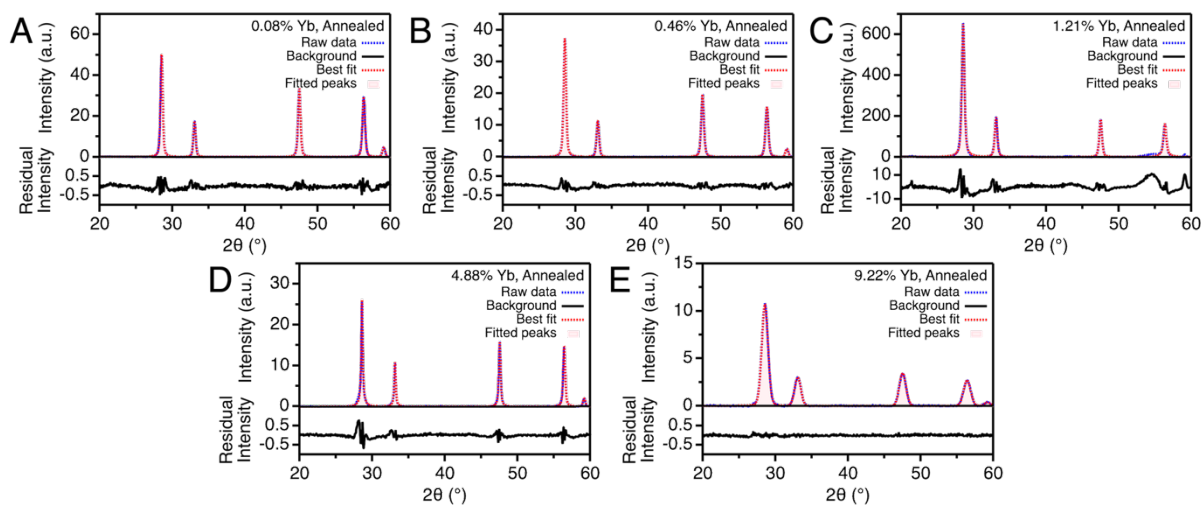


Figure 3.9. Multippeak pseudo-Voigt fits and residual fits for PXRD data of (A) 0.08%, (B) 0.46%, (C), 1.21%, (D) 4.88%, and (E) 9.22% annealed Yb^{3+} -doped CeO_2 .

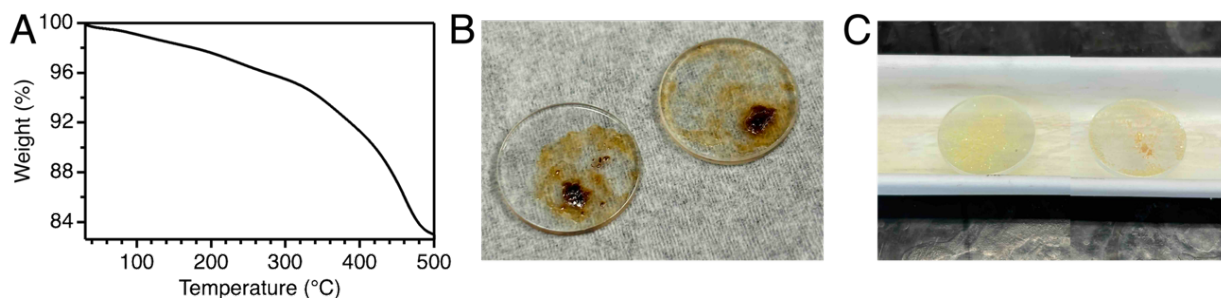


Figure 3.10. (A) TGA profile of as-synthesized $\text{CeO}_2:\text{Yb}^{3+}$, (B) photo of as-synthesized $\text{CeO}_2:\text{Yb}^{3+}$ drop-cast onto sapphire disks, (C) photo of $\text{CeO}_2:\text{Yb}^{3+}$ after annealing at 700 °C for 2 hours.

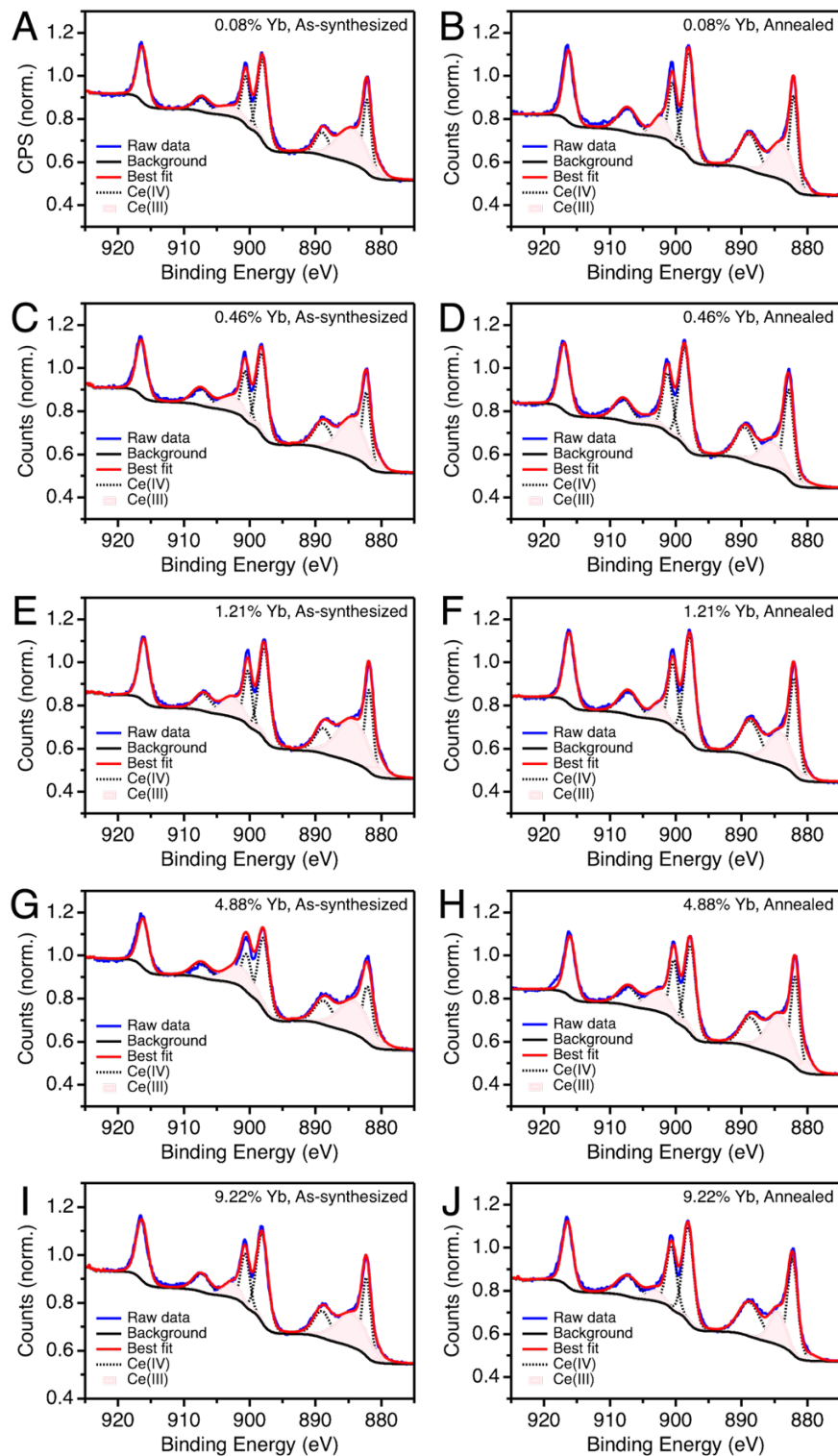


Figure 3.11. High-resolution Ce 3d XPS spectra of as-synthesized (A) 0.08%, (C) 0.46%, (E) 1.21%, (G) 4.88%, (I) 9.22% Yb³⁺-doped CeO₂ and annealed (B) 0.08%, (D) 0.46%, (F) 1.21%, (H) 4.88%, (J) 9.22% Yb³⁺-doped CeO₂. See Appendix for all fitting tables.

Room-temperature PL data for the annealed nanocrystals as a function of Yb^{3+} concentration are shown in **Figure 3.12**. We repeated the CeO_2 -sensitized excitation of Yb^{3+} at 300 K using a broadband xenon arc lamp set to 320 nm and confirmed the expected improvements in the signal-to-noise for both the PL and TRPL. We attribute these improvements to a reduction in defects, such as Ce^{3+} and oxygen vacancies, that cause unwanted non-radiative decay. In addition, it is suggested that Yb^{3+} ions migrate during annealing, decreasing the concentration of Yb^{3+} ions present in clusters and on the surface (*vide infra*).⁴¹

After confirming the improvements induced by annealing using indirect photoexcitation ($\lambda_{\text{ex}} = 320$ nm) at room temperature, we measured the Yb^{3+} TRPL with direct excitation ($\lambda_{\text{ex}} = 965\text{--}966$ nm, $\lambda_{\text{em}} = 1039$ nm) at 4 K (**Figure 3.13A**, **Table 3.3**). These data show significantly improved signal-to-noise and extended lifetimes, which fit well to monoexponential decay profiles up to 1.21% Yb^{3+} . The variable temperature (VT) TRPL data in **Figure 3.13B** show that lowering the temperature from 300 K to 4 K results in a substantial increase in the lifetime from 1.36 ms to 2.53 ms at the lowest dopant concentration, **0.08% Yb**. VT-TRPL data for the other Yb concentrations are shown in **Figure 3.14**.

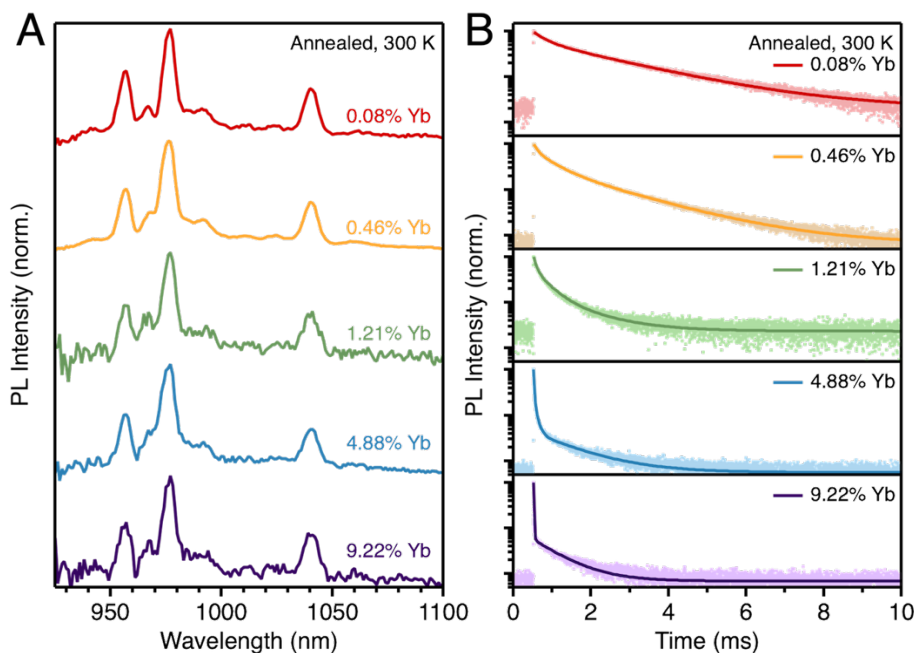


Figure 3.12. (A) PL and (B) TRPL of annealed Yb^{3+} -doped CeO_2 measured at 300 K via indirect excitation at $\lambda_{\text{ex}} = 320$ nm. TRPL measurements were performed using a xenon μs flash lamp.

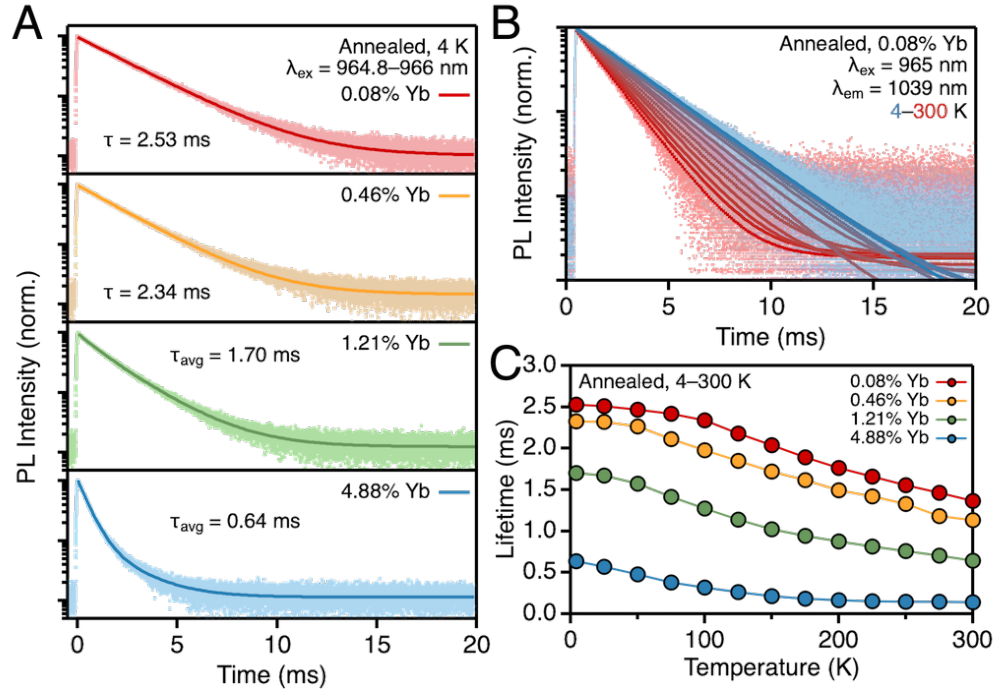


Figure 3.13. (A) TRPL of annealed CeO₂:Yb³⁺ samples at 4 K using direct excitation at $\lambda_{\text{ex}} = 965\text{--}966$ nm ($\lambda_{\text{em}} = 1039$ nm). (B) Representative VT-TRPL of **0.08% Yb** using direct excitation at $\lambda_{\text{ex}} = 965$ nm ($\lambda_{\text{em}} = 1039$ nm) and (C) lifetimes of annealed CeO₂:Yb³⁺ samples from 4 K to 300 K.

Table 3.3. Mono and biexponential fits for TRPL of annealed Yb³⁺-doped CeO₂ via indirect excitation ($\lambda_{\text{ex}} = 965\text{--}966$ nm, $\lambda_{\text{em}} = 1039$ nm) at 4 K.

Sample	A ₁	τ_1 (ms)	A ₂	τ_2 (ms)	τ_{avg} (ms)
0.08% Yb	0.960	2.530	—	—	—
0.46% Yb	0.947	2.339	—	—	—
1.21% Yb	0.269	0.908	0.671	2.02	1.699
4.88% Yb	0.909	0.501	0.117	1.75	0.643

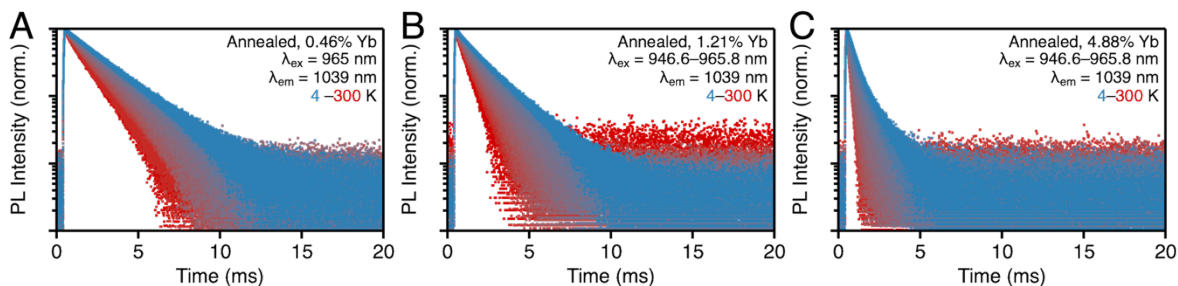


Figure 3.14. Variable temperature TRPL of (A) 0.46%, (B) 1.21%, and (C) 4.88% annealed Yb³⁺-doped CeO₂.

Figure 3.15A shows low-temperature PL spectra of annealed CeO₂:Yb³⁺ collected using 915 nm excitation. The spectra reveal an interesting trend: as the Yb³⁺ concentration increases, peak intensities at 965 nm and 972 nm decrease and increase, respectively. This observation suggests the presence of two emissive Yb³⁺ sites contributing to the spectrum. By varying the Yb³⁺ density in the lattice, we can manipulate the ratio of PL from these two sites, yielding distinct emission spectra. Our observation was confirmed by measurement of PL excitation (PLE) spectra for these samples, which revealed changes in relative intensity around 905 nm and 925 nm, highlighted in grey in **Figure 3.15B**, that we attribute to the changing ratio of two different Yb³⁺ site populations within the CeO₂ lattice. When excited at 905 nm, assigned as **Site A**, the PL spectrum shows its highest intensity at 965 nm and a weaker peak at 1039 nm. Excitation at 925 nm gives the spectrum of **Site B**, which shows its highest intensity at 972 nm and two smaller features at 1028 and 1038 nm that overlap with the strong 1039 nm **Site A** peak. Both spectra are isolated in **Figure 3.15C**. As for the as-synthesized samples, we see peaks corresponding to both **Site A** and **Site B**, however there is a broad signature with at least three peaks around where **Site B** emits, which may be due to variations in the orientation of the **Site B** Yb³⁺ that are resolved into a single **Site B** orientation after annealing (**Figure 3.16**).

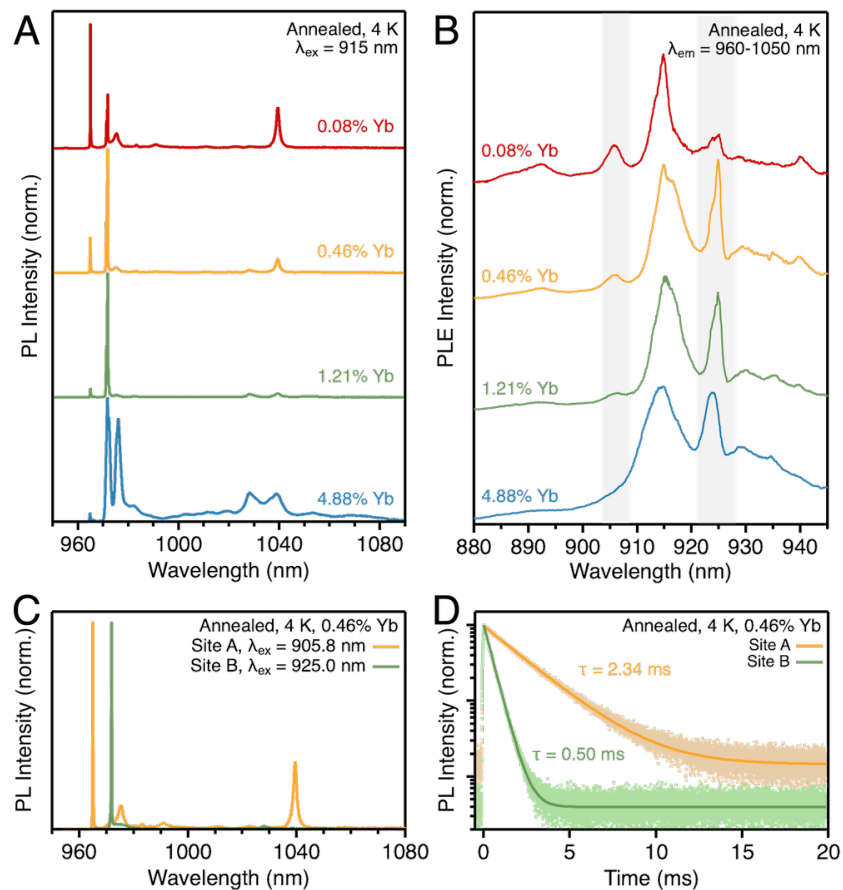


Figure 3.15. (A) PL and (B) PLE of annealed $\text{CeO}_2:\text{Yb}^{3+}$ at 4 K. Shaded regions show changes in the intensity of ~ 905 nm and ~ 925 nm PL features as the Yb^{3+} concentration changes. Overlay of (C) PL and (D) TRPL of Yb^{3+} **Site A** ($\lambda_{\text{ex}} = 965$ nm; $\lambda_{\text{em}} = 1039$ nm) and **Site B** ($\lambda_{\text{ex}} = 972$ nm; $\lambda_{\text{em}} = 1028$ nm) in **0.46% Yb**.

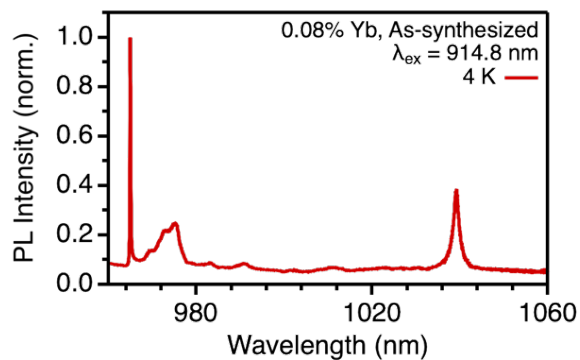


Figure 3.16. PL of as-synthesized 0.08% Yb^{3+} -doped CeO_2 at 4 K via direct excitation at $\lambda_{\text{ex}} = 915$ nm.

Table 3.4. Monoexponential fits for TRPL of annealed 0.46% Yb³⁺-doped CeO₂ via indirect excitation ($\lambda_{\text{ex}} = 965$ nm, $\lambda_{\text{em}} = 1039$ nm for Site A and $\lambda_{\text{ex}} = 972$ nm, $\lambda_{\text{em}} = 1028$ nm) at 4 K.

Sample	A ₁	τ_1 (ms)
Site A	0.947	2.339
Site B	0.997	0.496

When measuring TRPL of the lowest-energy f - f transitions from each site (1039 nm and 1028 nm for **Site A** and **Site B**, respectively) in the **0.46% Yb** sample, we observed that the **Site A** lifetime is approximately 5 $\times$ longer than the **Site B** lifetime (**Figure 3.15D**, **Table 3.4**). A similar 4 $\times$ lifetime difference between Yb³⁺ sites has been observed in Yb³⁺-doped CeO₂ using parallel factor analysis.⁴¹ In that work, one site had dominant peaks at 965 and 975 nm. The 965 nm peak is prominently observed in the PL spectrum of **Site A** (**Figure 3.15C**). The 975 nm peak is also observed in our **Site A** spectra, but it is much less intense than the other two features at 965 nm and 1039 nm. The second site showed a dominant peak at 972 nm,⁴¹ closely aligning with our observations.

Additional studies have used the characteristic peaks of Yb³⁺ to identify the specific crystal-field symmetries of the two Yb³⁺ sites (**Figure 3.17**).^{41,55} Specifically, they assign the 968 nm, 978 nm, and 1041 nm emission lines to a site with O_h symmetry and the 975 nm and 1031 nm emission lines to a site with C_{3v} symmetry.³⁹ Given the similarity in positions and intensities of our spectra to theirs, we can associate our **Site A** spectrum (965, 975, and 1039 nm emission lines) with the O_h site and our **Site B** spectrum (971 nm and 1028 nm emission lines) with the C_{3v} site. We note that previous work differentiated between two types of C_{3v} sites, one formed by vacancy of the nearest O²⁻ anion proximal to the Yb³⁺ and one formed by an OH⁻ group substituting for an O²⁻ anion proximal to the Yb³⁺, but these cannot be confidently differentiated in our PL spectra (*vide infra*). Finally, it is worth mentioning that tetragonal (C_{4v}) Yb³⁺ sites have also been reported in cerium oxide,³⁹ but this site is not observed in our samples.

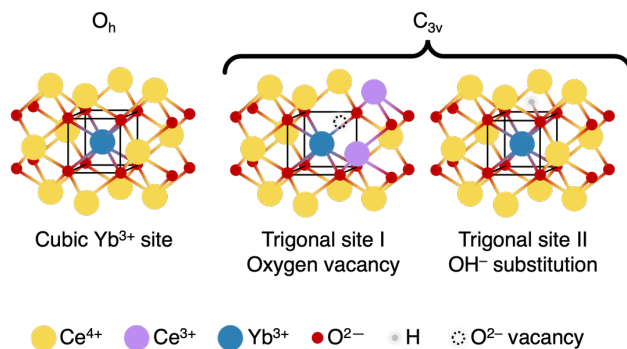


Figure 3.17. Schematic representation of local Yb^{3+} site geometries with possible arrangements demonstrating octahedral (O_h) and trigonal (C_{3v}) symmetries and associated distortions.

3.2.2 Electron Paramagnetic Resonance Spectroscopy of $\text{CeO}_2:\text{Yb}^{3+}$

We investigated the spin properties of the lowest-lying Kramers doublet of the $^2F_{7/2}$ level using EPR spectroscopy. Continuous-wave (CW) EPR spectra of the **0.46%** and **0.08% Yb** samples before and after annealing are shown in **Figure 3.18A-B**. We observe a characteristic Yb^{3+} feature at ~ 200 mT ($g \sim 3.42$) attributable to a cubic Yb^{3+} site of non-magnetic Yb^{3+} isotopes within the CeO_2 lattice, consistent with previous $\text{CeO}_2:\text{Yb}^{3+}$ EPR studies ($g \sim 3.43$).^{37,39,40} This line is flanked by hyperfine lines due to the magnetic isotopes ^{171}Yb (spin 1/2) and ^{173}Yb (spin 5/2).

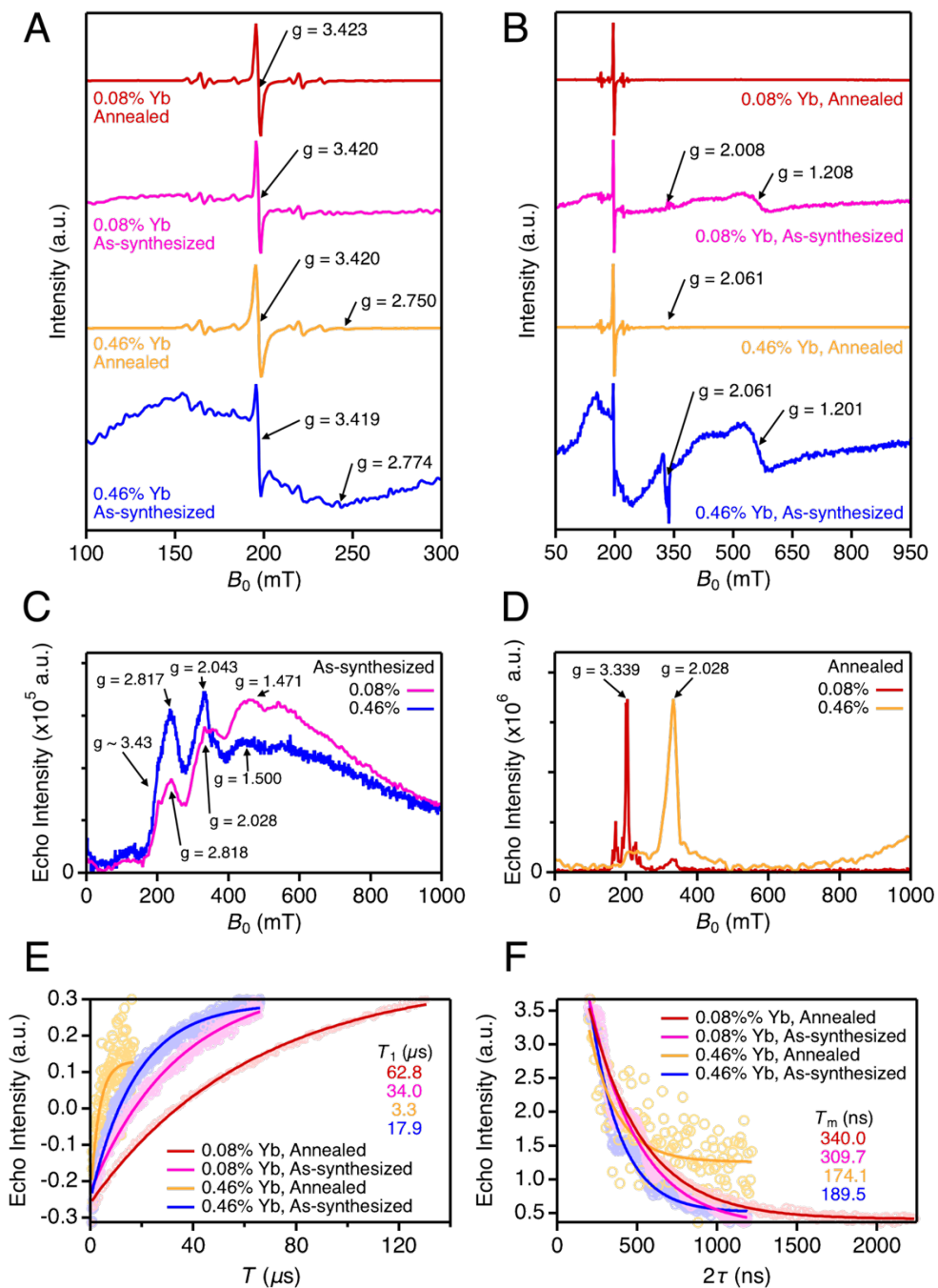


Figure 3.18. CW EPR (9.4 GHz, 5 K) spectra of (A) Yb^{3+} features and (B) CeO_2 defect features from as-synthesized and annealed **0.08% Yb** and **0.46% Yb** samples. Pulse EPR (9.7 GHz, 5 K) measurements including EDFS spectra of (C) as-synthesized and (D) annealed **0.08% Yb** and **0.46% Yb** samples, and (E) Inversion recovery and (F) Hahn echo decay of **0.08% Yb** and **0.46% Yb** samples at 202 mT.

Detailed EPR investigations of $\text{CeO}_2:\text{Yb}^{3+}$ have identified two types of trigonal sites that are formed by defects in bulk $\text{CeO}_2:\text{Yb}^{3+}$ crystals, trigonal site I ($g_{\perp} = 2.744$, $g_{\parallel} = 4.733$), due to an adjacent oxygen vacancy, and trigonal site II ($g_{\perp} = 3.060$, $g_{\parallel} = 4.152$), due to OH^- in place of an adjacent O^{2-} ion.^{37,40,38,56,57} The $g_{\perp}$ features are generally more pronounced than the $g_{\parallel}$ features. We observe the trigonal site I ($g \sim 2.76$) only in the **0.46% Yb** sample, indicating a higher density of oxygen vacancies at increased Yb^{3+} concentrations. There is no clear evidence of Yb^{3+} in trigonal site II, but detection of trigonal site II is complicated by overlap with ^{171}Yb hyperfine lines. Simulated EPR spectra including trigonal sites I and II are shown in **Figure 3.19**. Previously, we noted that **Site B** cannot be assigned to a specific trigonal site based on our PL data. However, we see an increase in **Site B** intensity from **0.08% Yb** to **0.46% Yb**, similar to that of trigonal site I, suggesting that **Site B** is associated with trigonal site I.

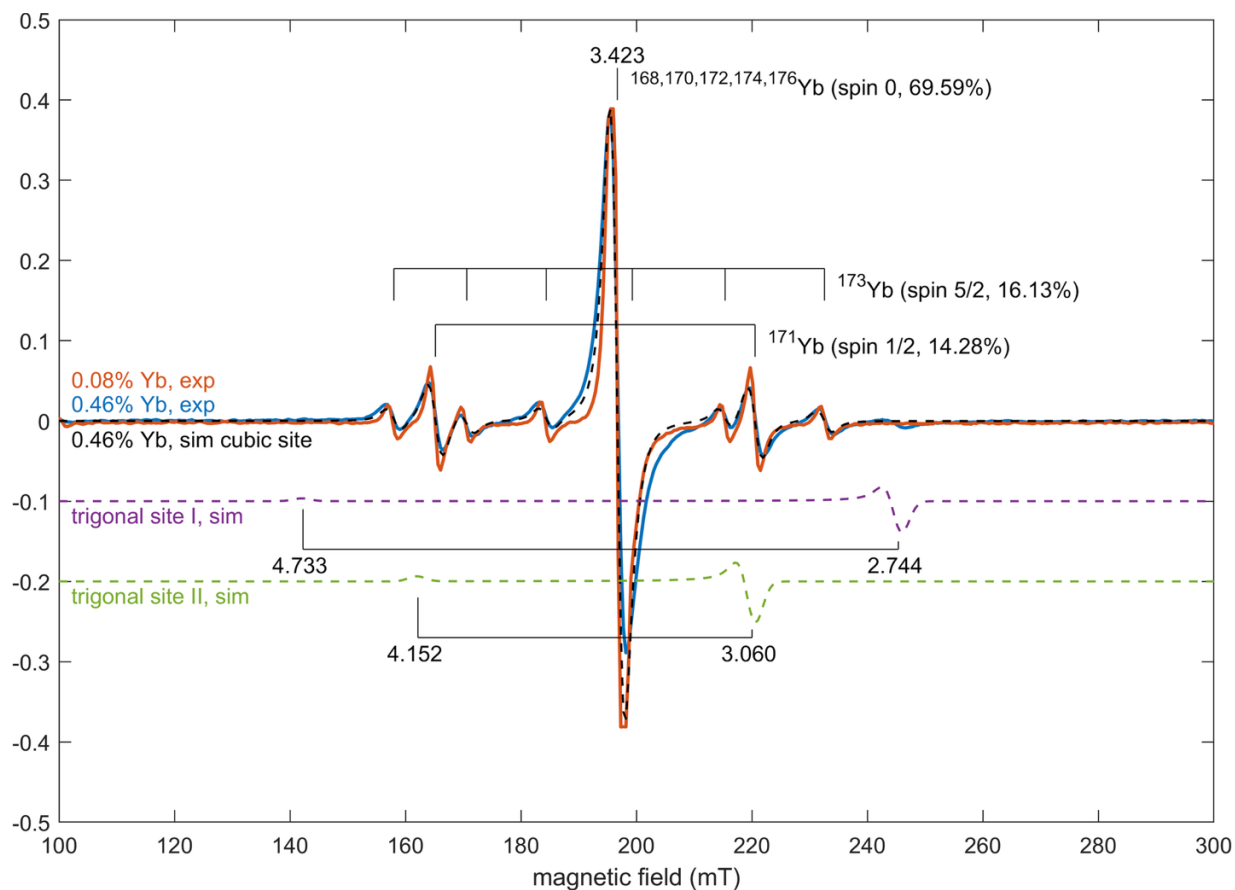


Figure 3.19. Experimental and simulated X-band CW EPR spectra of Yb^{3+} -doped CeO_2 . Experimental spectra (blue and red) were recorded at 5 K, $\nu_{\text{mw}} = 9.42$ GHz, and 48 dB attenuation. The spectra are almost entirely due to Yb^{3+} in cubic sites. Spectral fitting of the 0.08% $\text{CeO}_2\text{:Yb}^{3+}$ spectrum (black dashed) gives the following spin Hamiltonian parameters: isotropic $g = 3.423(6)$, isotropic $A(^{171}\text{Yb}) = 2.603(20)$ GHz, and isotropic $A(^{173}\text{Yb}) = 0.7135(60)$ GHz. The six ^{173}Yb hyperfine lines are not equally spaced and not centered around the field corresponding to the g value due to second-order effects resulting from the large hyperfine couplings relative to the Zeeman splitting. Simulations for the two known trigonal sites using g values from literature are included as well (purple and green dashed).³⁸ No $^{171}\text{Yb}/^{173}\text{Yb}$ hyperfine couplings were included for the trigonal site simulations. A small contribution from trigonal site I is visible in the blue experimental spectrum at 245 mT. No contribution from trigonal site II can be discerned. Their observation is complicated by spectral overlap with the ^{171}Yb hyperfine lines.

The feature at 335 mT ($g \sim 2$) in the **0.46% Yb** samples (**Figure 3.18B**) and the **0.08% Yb** as-synthesized sample is hypothesized to be indicative of adsorbed superoxo species, O_2^- , with one unpaired electron (g values ranging from 2.005–2.05), either adsorbing to Ce^{4+} ions or filling O^{2-} vacancies, as described by several prior studies.^{58,59,60} The other significant feature in **Figure 3.18B** at ~560 mT ($g \sim 1.20$) has been correlated to a nearly cubic Ce^{3+} site, with Constantini and coworkers demonstrating that the site symmetry has slight g -factor anisotropy and yields a range of g values from 1.14 to 1.44 due to the presence of distant defects (the homogeneous cubic site has $g = 1.266$ at 4.2 K).⁶¹ After annealing, the intensity of this feature is significantly reduced, in agreement with the observed decrease in Ce^{3+} concentration by XPS (**Figure 3.8**). It is worth noting that the Ce^{3+} resonance is often incorrectly associated with a feature at $g = 1.96$ – 1.97 due to an electron trapped in an oxygen vacancy.^{61,62} These observations are consistent with an increase in charge compensation from the charge mismatch created by the substitution of Yb^{3+} on the native Ce^{4+} sites. Annealing significantly reduces the concentrations of Ce^{3+} and O_2^- spin centers, while the signal of Yb^{3+} in cubic sites noticeably increases.

Echo-detected field-sweep (EDFS) spectra of the as-synthesized samples yield additional insight. We observed the characteristic Yb^{3+} feature at 202 mT ($g \sim 3.43$) as a shoulder of the second peak within a series of overlapping broad peaks at 110, 230, 350, 460, and 550 mT (**Figure 3.18C**). These broad peaks have not been fully identified in the literature, but we note them as possible defects that merit further investigation. Interestingly, as shown in **Figure 3.18D**, the difference between the annealed **0.08% Yb** and **0.46% Yb** samples becomes very prominent in the EDFs. The **0.08% Yb** has a sharp 201 mT peak ($g = 3.339$) while the **0.46% Yb** sample is dominated by a 350–360 mT peak with a small peak at 201 mT. The 360 mT feature is associated with the previously mentioned adsorbed superoxo species O_2^- (g values ranging from 2.005–2.05). We also note that the signal at 201 mT increased upon annealing in **0.08% Yb** but decreased with annealing in **0.46% Yb**. The decrease after annealing in **0.46% Yb** contrasts with the increase in the CW EPR signal, which is less limited by spin coherence and relaxation times.

For quantum applications, long electron spin coherence times are desired. We therefore probed the phase memory times (T_m) in these samples via Hahn echo decays and the longitudinal spin relaxation time

T_1 via inversion recovery. The phase memory time is determined by several decoherence mechanisms and is ultimately limited by T_1 . Large T_1 and T_m are critical for qubit fidelity.⁶³ For the **0.08% Yb** samples, the annealed sample shows a longer T_1 (62.7 μ s) than the as-synthesized sample (33.9 μ s) (**Figure 3.18E**). However, comparable T_m values for the annealed (339 ns) and as-synthesized (309 ns) samples (**Figure 3.18F**) suggest that although T_1 doubles, annealing may not yield a corresponding improvement in coherence times. This result implies that the dominant decoherence pathway is dephasing due to fluctuating local fields, such as Yb-Yb interactions, residual paramagnetic surface defects, adsorbed superoxo species, local symmetry variations, or other sources of spectral diffusion, rather than T_1 relaxation of excited spins. Additionally, as the Yb³⁺ concentration increases to 0.46%, we see much shorter T_1 and T_m lifetimes for both as-synthesized and annealed samples. Due to the low signal-to-noise ratio of the data from the annealed **0.46% Yb** sample, no clear annealing effects are observed in the T_1 or T_m at this Yb³⁺ concentration.

In both the **0.08%** and **0.46%** as-synthesized samples, their echo decays show electron spin echo envelope modulation (ESEEM) oscillations of 8.6(2) MHz and 8.8(2) MHz, respectively (**Figure 3.20**); these modulations are ascribed to ¹H, which has a Larmor frequency of 8.60 MHz at 202 mT. The ¹H modulations disappear after annealing, suggesting that they originate from the oleylamine ligands that are burnt off during annealing. In comparison to previously reported CeO₂:Er³⁺ nanocrystal studies, ensembles of ~7 nm nanocrystals doped with an estimated 13.2–0.3 Er³⁺ ions per nanocrystal were demonstrated to have T_m lifetimes of ~170–780 ns, and thin-films of CeO₂:Er³⁺ at single ppm concentrations have reported T_m lifetimes of ~0.7–38.8 μ s or longer with different pulse sequences.^{9,33,34} While our 0.08% Yb sample is significantly higher in Yb³⁺ concentration, our coherence lifetimes after annealing are similar to CeO₂:Er³⁺ nanocrystal ensembles reported at ~3 dopants per nanocrystal.⁹ Our data thus point to the possibility of improving upon the current metrics by further decreasing the Yb³⁺ concentration to single-digit numbers of atoms within each nanocrystal (**Table 3.5**).

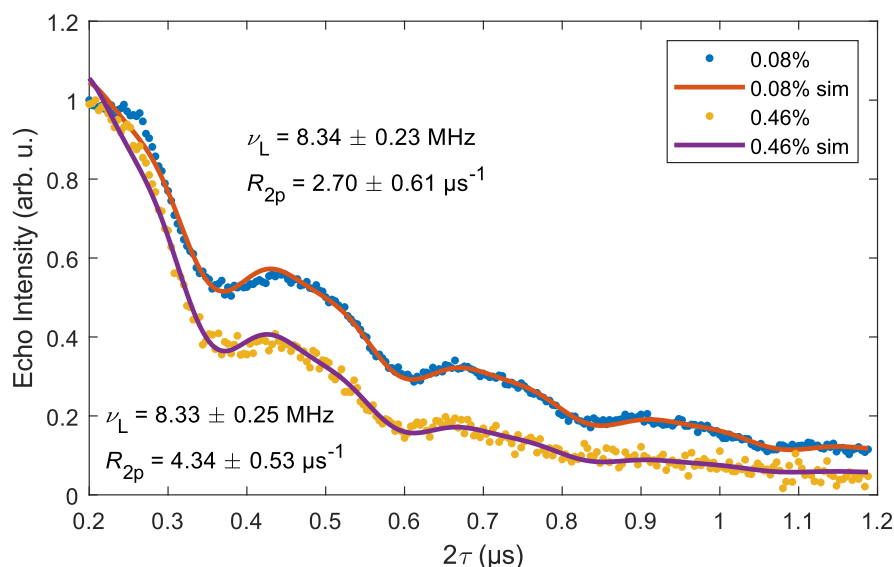


Figure 3.20. Two-pulse electron spin echo envelope modulation (ESEEM) of 0.08% and 0.46% as-synthesized $\text{CeO}_2\text{:Yb}^{3+}$ at 202 mT (5 K; 9.668 GHz for 0.08%, 9.672 GHz for 0.46%). Decays were fit with the following two-pulse ESEEM model for a $S=1/2$ electron spin center coupled to matrix $I=1/2$ nuclei, $V_{2p}(2\tau) = V_0 \left[1 - \frac{k}{4} (3 - 4 \cos(\omega_L \tau) + \cos(2\omega_L \tau)) \right] \exp(-R_{2p} 2\tau) + C$, where V_0 is the overall amplitude, k is the modulation depth, ω_L is the ^1H Larmor frequency ($\omega_L/2\pi = \nu_L = 8.60$ MHz at 202 mT), R_{2p} is the decay rate constant of the echo, and C is an offset. The modulation depths are 14-18%.

Table 3.5. Summary of optical and spin lifetime values at 4 K. Optical lifetimes were collected via direct excitation ($\lambda_{\text{ex}} = 965\text{-}966$ nm).

Sample	As-synthesized			Annealed		
	PL	EPR		PL	EPR	
	T_1 (ms)	T_1 (μs)	T_m (ns)	T_1 (ms)	T_1 (μs)	T_m (ns)
0.08%	2.01	34.0	309.7	2.53	62.8	340
0.46%	—	17.9	174.1	2.34	3.3	189.5
1.21%	—	—	—	1.70	—	—
4.88%	—	—	—	0.64	—	—

3.3 Conclusion

In conclusion, we report a systematic investigation of Yb^{3+} as an optically active and spin-bearing dopant within nanocrystalline CeO_2 . We observed that Yb^{3+} incorporation is near stoichiometric from 10% to 0.01% Yb; however, the accompanying oxygen vacancies, surface effects arising from the nanocrystal size, and the presence of Ce^{3+} result in poorly emitting nanocrystals in the as-synthesized state. Investigation of the Yb^{3+} PL revealed the presence of efficient non-radiative decay processes that compete with the desired PL, even at low temperatures. EPR measurements at 4-5 K indicate the presence of oxygen vacancies in close proximity to Yb^{3+} centers, which not only reduce the cubic site symmetry but may also facilitate unwanted non-radiative decay. After annealing at 700 °C for 2 h, the nanocrystal quality is significantly improved. We observed a decrease in Ce^{3+} concentration by XPS and improved signal-to-noise in the PL spectra, indicating that annealing helps mitigate the defects interacting with Yb^{3+} . However, pulse EPR measurements show that although annealing improves the spin lifetime (T_1), the coherence lifetime (T_m) is largely unaffected and may be limited by fluctuating local fields that dephase the electron spins.

As CeO_2 gains increasing attention as a promising host lattice for quantum information processing, this work highlights several complicating aspects of its nanocrystalline structure and identifies annealing as one common experimental handle that can be used to control them. By combining low-temperature PL with CW and pulse EPR data on $\text{CeO}_2\text{:Yb}^{3+}$ nanocrystals, we directly connect dopant concentration and host-defect chemistry to qubit-relevant optical and spin-relaxation metrics, establishing quantitative benchmarks and a defect-engineering roadmap for scalable rare earth spin qubits in wide-bandgap colloidal hosts. To address the remaining challenges with limited coherence beyond low dopant concentrations, it is suggested that exploring alternative synthesis methods that yield CeO_2 with fewer paramagnetic Ce^{3+} sites, removal of surface species and defects with higher temperature annealing or additional encapsulation of the nanocrystals in a matrix or shell, and higher precursor purity are possible handles to improve the current benchmarks. While these defects do not preclude the use of CeO_2 as a qubit platform, addressing the

complexity within this system will require further investigation into defect formation and tunability to fully leverage CeO₂ for quantum applications.

3.4 *Experimental Methods*

3.4.1 *General Methods and Materials*

All synthetic preparations were performed in ambient air in a well-ventilated fumehood or on a benchtop unless otherwise stated. All chemicals listed below were used without further purification unless stated otherwise. Cerium(III) nitrate hexahydrate ($\geq 99\%$ trace metals basis), ytterbium(III) nitrate pentahydrate ($\geq 99.9\%$ trace metals basis), oleylamine (technical grade, 70%), 1-octadecene (technical grade, 90%), toluene (ACS reagent, $\geq 99.5\%$), hexanes (ReagentPlus, $\geq 99\%$), methanol (ReagentPlus, $\geq 99\%$) and acetone (ACS reagent, $\geq 99.9\%$) were all purchased from Millipore Sigma.

3.4.2 *Synthesis of CeO₂:Yb³⁺ nanocrystals*

As described by Lee et al.,⁴² cerium(III) nitrate hexahydrate ($1-x$ mmol) and ytterbium(III) nitrate pentahydrate (x mmol, $x = 0.1, 0.05, 0.01, 0.005, 0.001$) were added to a 50 mL 3-neck round bottom flask equipped with a condenser, thermal probe, and stir bar. For the 0.005 and 0.001 mmol quantities, a stock solution of ytterbium(III) nitrate pentahydrate was dissolved in a known volume of methanol, which was then transferred as a μL volume to the reaction flask according to the desired ytterbium concentration. Oleylamine (0.98 mL, 3 mmol) and 1-octadecene (4 g, 5.07 mL) were added to the mixture, forming a clear solution. The mixture was heated to 80 °C while stirring, turning into a clear yellow solution, and held at 80 °C for 30 minutes. Then, the temperature was quickly ramped to 260 °C and held for 2 hours, turning into a dark brown solution, then cooled to room temperature. The reaction mixture was purified by a series of centrifugation steps. First, the crude reaction mixture was transferred to a Falcon tube and precipitated

using ~30 mL of acetone, followed by centrifugation at 8000 rpm for 10 min. The supernatant (typically a clear light brown on the first crash out) was poured off and the pellet was redissolved in hexanes. The solution was crashed out twice more with additional acetone. The final pellet was redissolved in hexanes. The particle solution in hexanes is used for TEM sample preparation, XPS sample preparation, XRD sample preparation, and PL/PLE/TRPL sample preparation.

3.4.3 Instrumentation and Characterization Methods

Transmission electron microscopy (TEM) images were obtained with a FEI Tecnai G2 F20 SuperTwin microscope operated at 200 kV using bright field imaging. All samples were prepared by drop-casting 5 μ L of sample dissolved in hexanes onto a suspended ultrathin carbon film on lacey carbon support film, 400 mesh, copper grids purchased from Ted Pella, Inc. The samples were allowed to dry in air for 5 min until the hexanes evaporated. All grids were placed under vacuum overnight to ensure complete dryness before imaging.

Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 Discover diffractometer at 50 kV with 1000 μ A via a Cu anode microfocus X-ray source ($\lambda = 1.5406 \text{ \AA}$) and a Pilatus 100K large-area detector. The beam for the measurement was collimated to a 1 mm beam diameter, and collection times were 30–90 s per step ($5.5^\circ 2\theta$ step size). Raw diffraction data were processed using Bruker DIFFRAC.EVA software, and peaks were fitting with Pseudo-Voigt multipeak functions using Python.⁴³ As-synthesized samples were prepared by repeatedly drop-casting 5 μ L of sample suspended in hexanes onto a Si wafer to build up a thick film of sample. Annealed samples were prepared by the same method as as-synthesized samples and then annealed under a furnace at 700 $^\circ$ C for 2 h.

Elemental analysis was performed by inductively coupled plasma-optical emission spectroscopy (ICP–OES) on a Perkin Elmer Optima 3000. Samples were digested for 48 h in a 1:1 conc. $\text{H}_2\text{O}_2/\text{HNO}_3$ (concentrated) then filtered through a PTFE filter and diluted to 2% HNO_3 for analysis.

Thermogravimetric analysis (TGA) data were collected on a TA Instruments TGA Q5000 under ambient atmosphere at a scan rate of 10 $^\circ$ C/min.

Annealing was performed in a quartz tube using a Lindberg/Blue M Mini-Mite Tube Furnace with ambient air flow. The temperature was raised to 700 °C at a rate of 10 °C/min and kept at 700 °C for 2 h.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis-Ultra DLD spectrometer. This instrument has a monochromatized Al K α X-ray and a low energy electron flood gun for charge neutralization. X-ray spot size for these acquisitions was on the order of 700 x 300 μ m. The electrostatic lens was used for data collection. Pressure in the analytical chamber during spectral acquisition was less than 5×10^{-9} Torr. Pass energy for survey spectra (composition) was 160 eV. Pass energy for the high-resolution spectra was 40 eV. The take-off angle (the angle between the sample normal and the input axis of the energy analyzer) was 0° (0-degree take-off angle $\sim$ 100 Å sampling depth). The Kratos Vision2 software program was used to determine peak areas and to calculate the elemental compositions from peak areas. CasaXPS was used to peak fit the high-resolution spectra. For the high-resolution spectra, a Shirley background was used, and all binding energies were referenced to the C 1s C-C bonds at 285.0 eV. As-synthesized samples were prepared by repeatedly drop-casting 5 μ L of sample suspended in hexanes onto a Si wafer to build up a thick film of sample. Annealed samples were prepared by the same method as as-synthesized samples and then annealed under a furnace at 700 °C for 2 h.

UV-visible (UV-vis) absorption measurements were collected on an Agilent Cary 5000 UV-Vis-NIR spectrophotometer in dual beam mode. All UV-vis data were collected by solid state measurements of samples drop-casted onto fused silica windows.

Room temperature photoluminescence (PL), photoluminescence excitation (PLE), and time-resolved photoluminescence (TRPL) measurements were collected on an Edinburgh FLS1000 photoluminescence spectrometer equipped with a 450 W ozone-free Xenon arc lamp, a microsecond Xenon flashlamp, and an NIR PMT (PMT-1700). All PL, PLE, and TRPL data were collected using samples drop-cast onto fused silica substrates.

Variable temperature photoluminescence (PL) measurements were performed by drop-casting the samples onto a sapphire disk, which was covered by a secondary sapphire disk and loaded into a closed-cycle helium cryostat. The sample was brought under high vacuum (10^{-6} Pa) and cooled to 4 K. Sample

emission was measured upon direct excitation of Yb^{3+} using a tunable continuous-wave Ti:sapphire laser with a spectral bandwidth of <0.01 nm, configured to lase in the 900-1000 nm range. The excitation wavelength was set to the $0 \rightarrow 2'$ transition (915 nm) as determined through PLE (see below). Sample emission was collected and focused into a monochromator with a spectral resolution of 0.02 nm. Spectra were recorded using a LN_2 -cooled silicon CCD camera. All spectra were corrected for instrument response.

Variable-temperature time-resolved photoluminescence (TRPL) measurements were performed using the same general setup as described above for variable-temperature PL measurements. Indirect excitation of the samples was performed using the third harmonic of a Nd:YAG laser at 355 nm with a pulse duration of 20 ps and a repetition rate of 50 Hz. TRPL measurements using direct excitation of Yb^{3+} were performed by passing the Ti:sapphire laser beam through an acousto-optic modulator (AOM). The excitation wavelength was set to the $0 \rightarrow 0'$ transition (~ 965 nm) as determined through PLE (see below) and was optimized at every temperature point to account for shifts in the excitation peak position. A DS345 function generator was used to provide a custom square wave input signal to the AOM to control laser *on*- and *off* times. Pulses were configured with an on time of 100 μs and a 50 Hz repetition rate. For both excitation schemes, sample emission was focused onto a monochromator (10.7 nm spectral bandwidth), collected on a LN_2 -cooled Hamamatsu InGaAs/InP NIR photomultiplier tube and sent to an SR430 photon counter to generate the TRPL data. Emission was monitored at the $0' \rightarrow 4$ transition (1039 nm) and a time resolution of 1.28 μs was used for data binning.

Low temperature photoluminescence excitation (PLE) measurements were performed using the same general setup as described above for variable temperature PL measurements. Using the CCD camera, emission spectra were collected every 200 ms while the Ti:sapphire excitation wavelength was continuously scanned at a rate of approximately 0.15 nm/s. The excitation wavelength and sample emission were captured simultaneously on the CCD, using a 950 nm long-pass filter to reduce the laser intensity on the detector. For every spectrum, the excitation wavelength was extracted by fitting the laser peak with a Gaussian function. Sample emission in the 960-1050 nm range was integrated for every spectrum to provide

the corresponding PLE intensity. The resulting PLE spectrum was corrected for laser output power at every point.

Continuous-wave X-band (CW) electron paramagnetic resonance (EPR) spectra at 9.4 GHz and 5 K were collected on a Bruker EMX spectrometer equipped with a Bruker SHQE resonator and an Oxford Instruments ESR900 cryostat. Pulse X-band EPR experiments were performed at 9.7 GHz and 4 K on a Bruker ElexSys E580 spectrometer equipped with a 1 kW amplifier, a Bruker MD4 resonator, and an Oxford Instruments CF9350 cryostat. For both CW and pulse experiments the cryostats were cooled with liquid helium and the temperature was set with an Oxford Instruments ITC503 temperature controller. Pulse experiments used rectangular monochromatic 16 ns $\pi/2$ and 32 ns π pulses. Echo-detected field sweeps and Hahn echo decay experiments were done with $\pi/2$ - τ - π - τ -echo pulse sequences. Inversion recovery experiments were done with a π - T - $\pi/2$ - τ - π - τ -echo pulse sequence. As-synthesized samples were prepared by diluting a sample into toluene and freezing the sample in LN2. Annealed samples were annealed as described above, the flakes/powder (few mg) were collected and dispersed with sonication to form a suspension in toluene followed by freezing the sample in LN2.

3.5 Appendix: X-ray Photoelectron Spectroscopy Data

Ce 3d XPS spectra were fit using reference spectra from Paparazzo et al.'s work on fitting Ce 3d spectra of Ce₂O₃ and CeO₂.⁵⁸

Table 3.6. High-resolution Ce 3d XPS fitting components of as-synthesized 0.08% Yb³⁺-doped CeO₂.

Name				Ce(IV)				Ce(III)			
	ν	u	ν''	u''	ν'''	u'''	ν^0	u^0	ν'	u'	
Position	882.2	900.6	889	907.31	898.04	916.34	880.57	898.87	884.46	902.7	
FWHM	1.52	1.52	2.42	2.71	1.85	1.85	1.84	1.84	5.44	5.44	

Area	9926.02	6617.34	4954.67	3369.18	13480.2	9220.46	1149.89	712.93	16829.04	4588.75
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Table 3.7. High-resolution Ce 3*d* XPS fitting components of annealed 0.08% Yb³⁺-doped CeO₂.

Name	Ce(IV)						Ce(III)			
	<i>v</i>	<i>u</i>	<i>v</i> ^{''}	<i>u</i> ^{''}	<i>v</i> ^{'''}	<i>u</i> ^{'''}	<i>v</i> ⁰	<i>u</i> ⁰	<i>v</i> [']	<i>u</i> [']
Position	882.1	900.5	888.81	907.31	898	916.3	880.09	898.39	884	902.2
FWHM	1.49	1.49	3.43	3.43	1.93	1.93	1	1	4.09	2.8
Area	12729.3	8486.2	11314.03	7693.54	18606.3	12726.71	636.94	394.9	13390.98	5276.82

Table 3.8. High-resolution Ce 3*d* XPS fitting components of as-synthesized 0.46% Yb³⁺-doped CeO₂.

Name	Ce(IV)						Ce(III)			
	<i>v</i>	<i>u</i>	<i>v</i> ^{''}	<i>u</i> ^{''}	<i>v</i> ^{'''}	<i>u</i> ^{'''}	<i>v</i> ⁰	<i>u</i> ⁰	<i>v</i> [']	<i>u</i> [']
Position	882.3	900.7	888.94	907.47	898.18	916.48	880.57	898.87	884.4	902.49
FWHM	1.54	1.54	3.16	3.16	1.92	1.92	1.95	1.95	4.59	4.59
Area	9715.38	6476.92	6856.73	4662.58	13519.56	9247.38	1502.28	931.42	15221.33	5924.04

Table 3.9. High-resolution Ce 3*d* XPS fitting components of annealed 0.46% Yb³⁺-doped CeO₂.

Name	Ce(IV)						Ce(III)			
	<i>v</i>	<i>u</i>	<i>v</i> ^{''}	<i>u</i> ^{''}	<i>v</i> ^{'''}	<i>u</i> ^{'''}	<i>v</i> ⁰	<i>u</i> ⁰	<i>v</i> [']	<i>u</i> [']
Position	882.86	901.26	889.5	908.01	898.65	916.95	882	900.3	885.3	903.9
FWHM	1.8	1.8	3.24	3.24	2.04	2.04	5.02	5.02	4.41	4.41
Area	15978.22	10652.14	10605.2	7211.53	20035.66	13704.39	2953.57	1831.21	11570.06	3150.4

Table 3.10. High-resolution Ce 3d XPS fitting components of as-synthesized 1.21% Yb³⁺-doped CeO₂.

Name	Ce(IV)						Ce(III)			
	v	u	v''	u''	v'''	u'''	v^0	u^0	v'	u'
Position	881.91	900.31	888.86	907.05	897.8	916.1	880.57	898.87	884.4	902.6
FWHM	1.5	1.5	3.02	3.02	1.94	1.94	2.5	2.5	5.56	4.02
Area	13881.22	9254.14	8717.52	5927.91	20247.89	13849.56	2752.9	1706.8	26795.24	8760.16

Table 3.11. High-resolution Ce 3d XPS fitting components of annealed 1.21% Yb³⁺-doped CeO₂.

Name	Ce(IV)						Ce(III)			
	v	u	v''	u''	v'''	u'''	v^0	u^0	v'	u'
Position	882.06	900.46	888.67	907.21	897.88	916.18	880.27	898.57	884.21	902.5
FWHM	1.67	1.67	3.48	3.48	1.97	1.97	1.97	1.97	4.06	2.67
Area	21702.16	14468.1	16775.72	11407.49	27843.94	19045.25	1494.84	926.8	18081.26	5581.47

Table 3.12. High-resolution Ce 3d XPS fitting components of as-synthesized 4.88% Yb³⁺-doped CeO₂.

Name	Ce(IV)						Ce(III)			
	v	u	v''	u''	v'''	u'''	v^0	u^0	v'	u'
Position	882.12	900.52	888.78	907.42	897.9	916.2	880.67	898.97	884.1	901.2
FWHM	1.88	1.88	3.25	3.25	1.97	1.97	3.24	3.24	5.4	5.4
Area	9066.83	6044.55	6642.92	4118.61	12224.56	8361.6	827.93	513.32	15200.58	9120.35

Table 3.13. High-resolution Ce 3*d* XPS fitting components of annealed 4.88% Yb³⁺-doped CeO₂.

Name	Ce(IV)						Ce(III)			
	<i>v</i>	<i>u</i>	<i>v''</i>	<i>u''</i>	<i>v'''</i>	<i>u'''</i>	<i>v</i> ⁰	<i>u</i> ⁰	<i>v'</i>	<i>u'</i>
Position	881.9	900.3	888.63	907.28	897.78	916.08	880.17	898.47	884.28	902.4
FWHM	1.61	1.61	3.43	3.43	1.94	1.94	2.15	2.15	4.52	4.52
Area	20580.49	13720.33	14181.93	9218.25	24492.4	16752.8	3681.09	2282.28	26389.75	13020.85

Table 3.14. High-resolution Ce 3*d* XPS fitting components of as-synthesized 9.22 % Yb³⁺-doped CeO₂.

Name	Ce(IV)						Ce(III)			
	<i>v</i>	<i>u</i>	<i>v''</i>	<i>u''</i>	<i>v'''</i>	<i>u'''</i>	<i>v</i> ⁰	<i>u</i> ⁰	<i>v'</i>	<i>u'</i>
Position	882.3	900.7	889.01	907.36	898.1	916.4	880.57	898.87	884.4	902.6
FWHM	1.58	1.58	3.02	3.02	2.06	2.06	1.29	1.29	5.63	3.1
Area	9688.97	6459.31	6330.48	4304.72	14316.83	9792.71	498.32	308.96	14601.25	3546.83

Table 3.15. High-resolution Ce 3*d* XPS fitting components of annealed 9.22 % Yb³⁺-doped CeO₂.

Name	Ce(IV)						Ce(III)			
	<i>v</i>	<i>u</i>	<i>v''</i>	<i>u''</i>	<i>v'''</i>	<i>u'''</i>	<i>v</i> ⁰	<i>u</i> ⁰	<i>v'</i>	<i>u'</i>
Position	882.28	900.68	888.81	907.31	898.13	916.43	879.76	898.06	884.56	903.16
FWHM	1.84	1.84	3.93	3.93	1.92	1.92	2.79	2.79	2.89	2.89
Area	14940.54	9960.36	11497.75	6898.65	15764.54	10782.95	1141.13	707.5	8243.06	2706.59

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Appendix A.

Erbium Doped CeO₂ Nanocrystals

A.1. Introduction

As elaborated in Section 1.3.2 on cerium oxide as a spin qubit host, several recent studies have examined Er³⁺-doped CeO₂ as a promising candidate for spin qubit systems.^{1,2,3,4} These studies predominantly focused on epitaxially grown single crystals of CeO₂:Yb³⁺ on silicon, with the exception of the study by Wang et al., examining colloidally stable ~7 nm oleic acid-capped CeO₂ nanocrystals. At the onset of my endeavors into this area of research, with the hopes of applying what knowledge I had learned about defect engineering of CeO₂, I embarked on studying possible routes towards new nanostructures and heterostructures of CeO₂ that may allow us to optimize the host lattice for appropriate embedding of the dopant within a lattice. In this appendix, I will discuss the routes we investigated to achieve this goal, starting with Section 1.2.1, where we examined synthetic handles for tuning CeO₂:Er³⁺ by size, morphology, and annealing, and their associated effects on the room-temperature CeO₂-sensitized Er³⁺ lifetimes. In Section 1.2.2, we discuss shelling CeO₂:Er³⁺ with dense silica shells to encapsulate the Er³⁺ dopant beyond the terminations of the CeO₂ lattice, thereby generating a heterostructure. Finally, in Section 1.2.3, we discuss the application of atomic layer deposition to address this issue by examining nanocrystals spin-coated into thin films and subsequently layered with deposited CeO₂ to encapsulate the erbium-doped nanocrystals. Finally, we conclude the preliminary work thus far and discuss possible future work to further investigate these materials.

A.2. Result and Discussion

A.2.1. Synthesis and Photoluminescence of Er^{3+} -Doped CeO_2 Nanocrystals

Using a previously reported thermal decomposition synthesis,⁵ we first investigated the impact of parameters mentioned in the original study to control particle size and the Er^{3+} lifetime (**Figure A.1A**). The original synthesis calls for 3 equivalents (eq.) of oleylamine, and we initially targeted a 1% Er^{3+} concentration that we could observe by room temperature PL and TRPL, which is used as a benchmark for comparing the quality of the nanocrystals via Er^{3+} emission at ~ 1530 nm. We anticipated that longer Er^{3+} lifetimes at similar concentrations would suggest better Er^{3+} site homogeneity and CeO_2 lattice quality similar to that of the Yb^{3+} -doped CeO_2 system. Using this method, we produce spherical nanocrystals containing 1.48% Er^{3+} as measured by ICP-OES, with a TRPL decay ($\lambda_{\text{ex}} = 320$ nm, $\lambda_{\text{em}} = 1530$ nm) that fits a monoexponential profile with a lifetime of 1.47 ms (**Figure A.1B**).

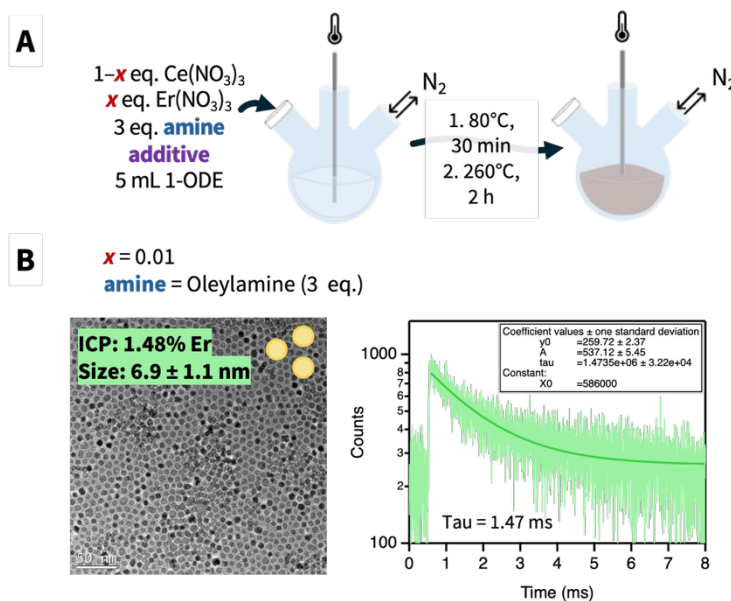


Figure A.1. (A) Diagram of thermal decomposition synthesis and parameters (bolded) that were investigated. (B) Resulting TEM, measured ICP-OES data of Er^{3+} concentration, size analysis, and TRPL data of the original synthesis targeting 1% Er^{3+} -doped CeO_2 using 3 eq. of oleylamine and no additive.

By altering the ligand composition from 3 eq. oleylamine to a mixture of 1.5 eq. oleylamine and 1.5 eq. octadecylamine, we observe a change in both the size and the shape of the nanocrystals, increasing from ~7 nm to ~13 nm; however, no longer appearing as monodisperse or spherical (**Figure A.2A**). We also observe that the PL lifetime collected by TRPL measurements significantly decreased as compared to the original synthesis, dropping from 1.47 ms to 0.75 ms. This is possibly due to the change in Er^{3+} concentration, as this increases from 1.48% to 1.73%, however, it may also be due to the change in the nanocrystal morphology, which appears to have lobes arising from the aggregation of smaller nanocrystals forming multi-particle aggregates. With the addition of distilled water (4 eq.) to the synthesis, we observe an increase in nanocrystal size with greater polydispersity; however, better retention of the spherical or polyhedral nanocrystal shape (less lobe-like character). We see the lifetime improves from the original synthesis from 1.47 ms to 1.70 ms. At this time, we are not able to resolve if the change in lifetime is solely from Er^{3+} concentration affects (where we anticipate a higher concentration of Er^{3+} is causing a lower lifetime) or if it is also due to nanocrystal quality, although it is likely at these relatively high Er^{3+} concentrations we are more likely to be limited by Er-Er interactions than lattice defects. Additional synthetic investigation would be necessary to validate this.

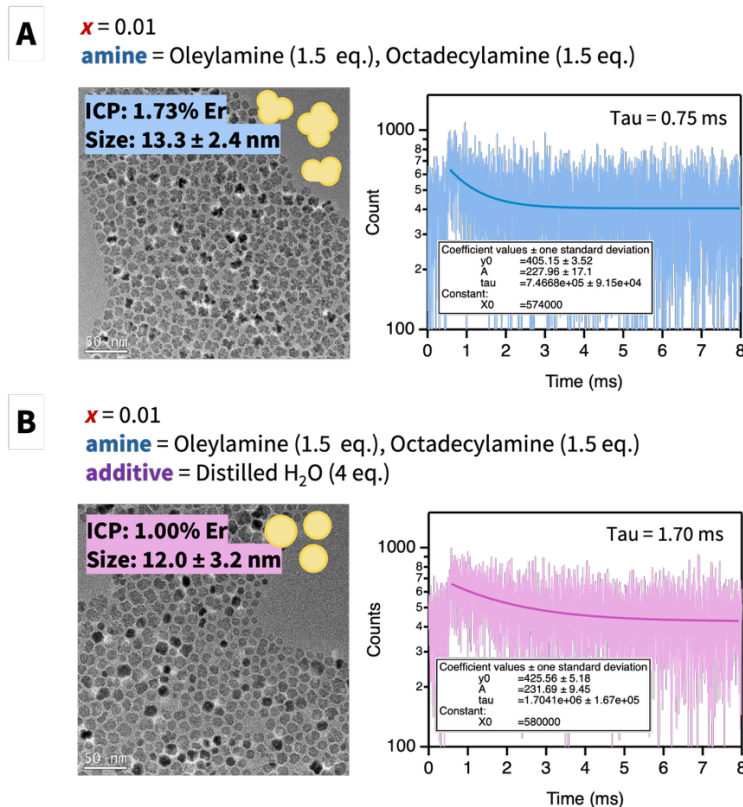


Figure A.2. TEM, Er³⁺ concentration, size analysis, and TRPL data of the synthesis targeting 1% Er³⁺-doped CeO₂ using (A) 1.5 eq. of oleylamine with 1.5 eq. of octadecylamine and (B) 1.5 eq. of oleylamine, 1.5 eq. of octadecylamine, with 4 eq. distilled H₂O.

One final set of syntheses was done to compare the reliability of this reaction at even lower concentrations of Er³⁺. We targeted 0.1% Er³⁺ in **Figure A.3**. In both syntheses, we achieve relatively similar nanocrystal sizes and the same measured Er³⁺ concentration by ICP-OES. This result is consistent with our earlier observation that as Er³⁺ concentration decreases, the PL lifetime increases. Here we see that the lifetimes have increased from ~1.5 ms at 1% Er³⁺ to ~2.5 ms at 0.1% Er³⁺. However, despite the same Er³⁺ concentration in these two samples, there is a 0.76 ms difference in PL lifetime. It is possible that the PL lifetime measured at room temperature likely has broad deviations in measurement and monoexponential fitting, given that the emission intensity for these materials overall are very low.

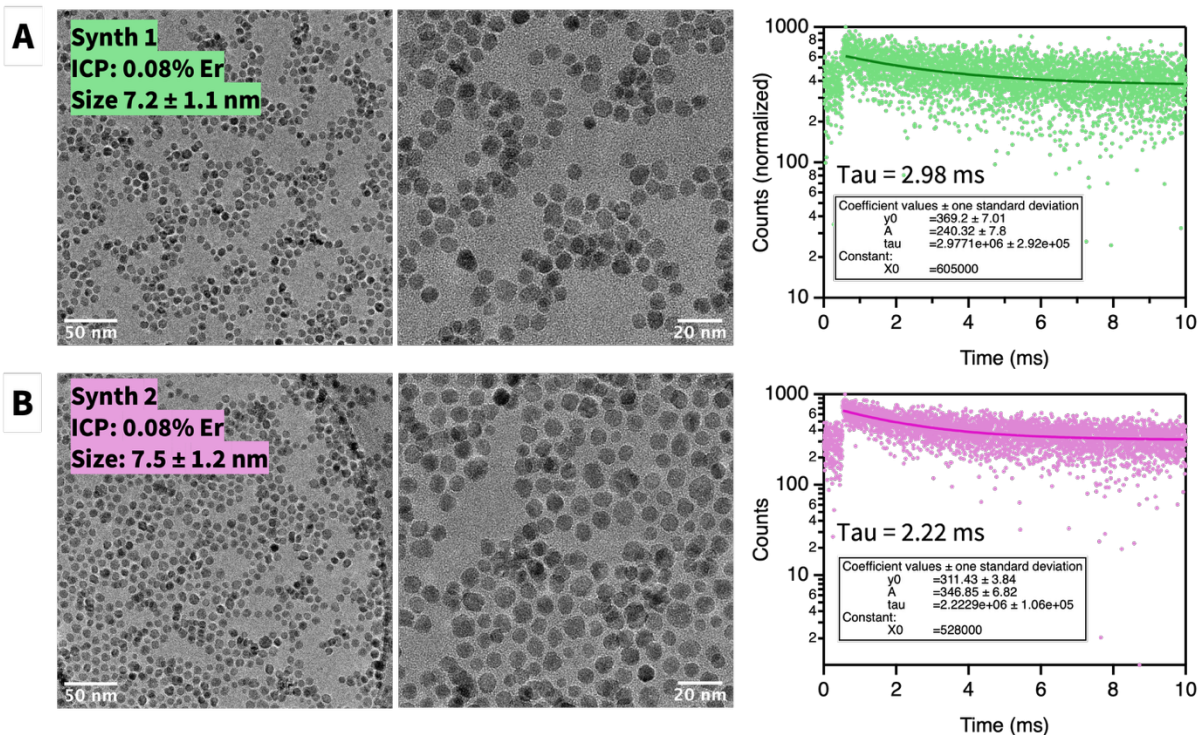


Figure A.3. TEM, Er^{3+} concentration, size analysis, and TRPL data of two identical syntheses, (A) synthesis 1 and (B) synthesis 2, targeting 0.1% Er^{3+} -doped CeO_2 .

Similar to our studies with $\text{CeO}_2\text{:Yb}^{3+}$, we also compared the impact of annealing at varying temperatures on the Er^{3+} lifetimes in our samples. When annealing both 1.5% Er and 0.08% Er samples at 500 °C for 2 hours under air, we observed an overall decrease in PL lifetimes as seen in **Figure A.4**, comparing two trials of the same test with the same sample to gauge variability in lifetimes and signal quality. While the exact PL lifetimes here are uncertain due to low signal-to-noise and insufficient decay time (samples were measured over 8 ms and could benefit from longer measurement time for more accurate lifetimes), the overall emissive signal quality is very low, and the signal-to-noise does not improve after annealing. As seen in Chapter 3, organic ligands are entirely removed by 500 °C; however, it appears that the Er^{3+} site homogeneity and lattice defects that are causing decay of signal do not significantly decrease after annealing.

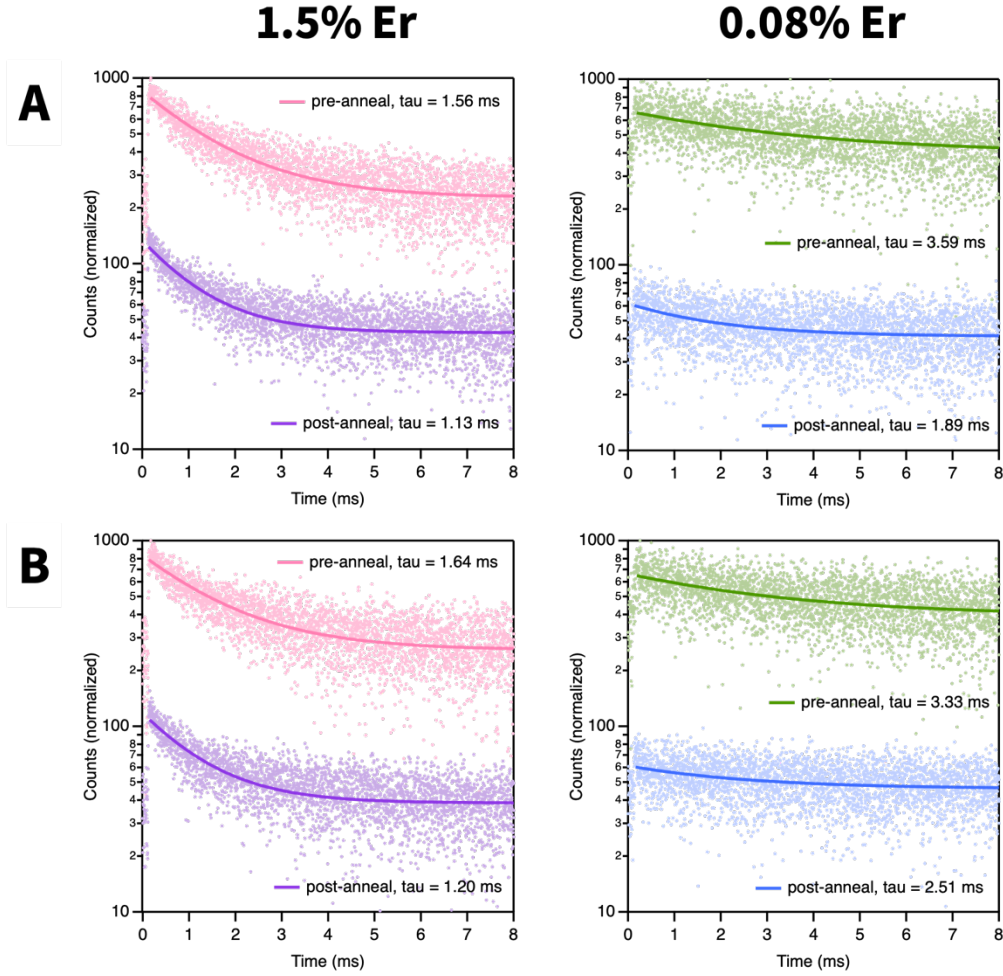


Figure A.4. 1.5% Er^{3+} -doped CeO_2 and 0.08% Er^{3+} -doped CeO_2 before and after annealing at 500 °C across (A) trial 1 and (B) trial 2.

When we compare this to annealing 1.2% Er^{3+} -doped CeO_2 at 700 °C for 2 hours in air, however, we do see a significant improvement in signal-to-noise ratios (**Figure A.5**). Across two separate trials of the same sample under the same annealing conditions, we are able to observe a significant improvement in signal-to-noise ratios for 1.22% Er^{3+} -doped CeO_2 . There is also an observed rise time in the TRPL data, suggesting possible measurement of the excited-state dynamics (energy transfer) from the CeO_2 lattice to Er^{3+} . Notably, the PL lifetimes do not significantly improve after annealing, likely because Er-Er interactions, rather than the host lattice quality, dominate the decay profile.

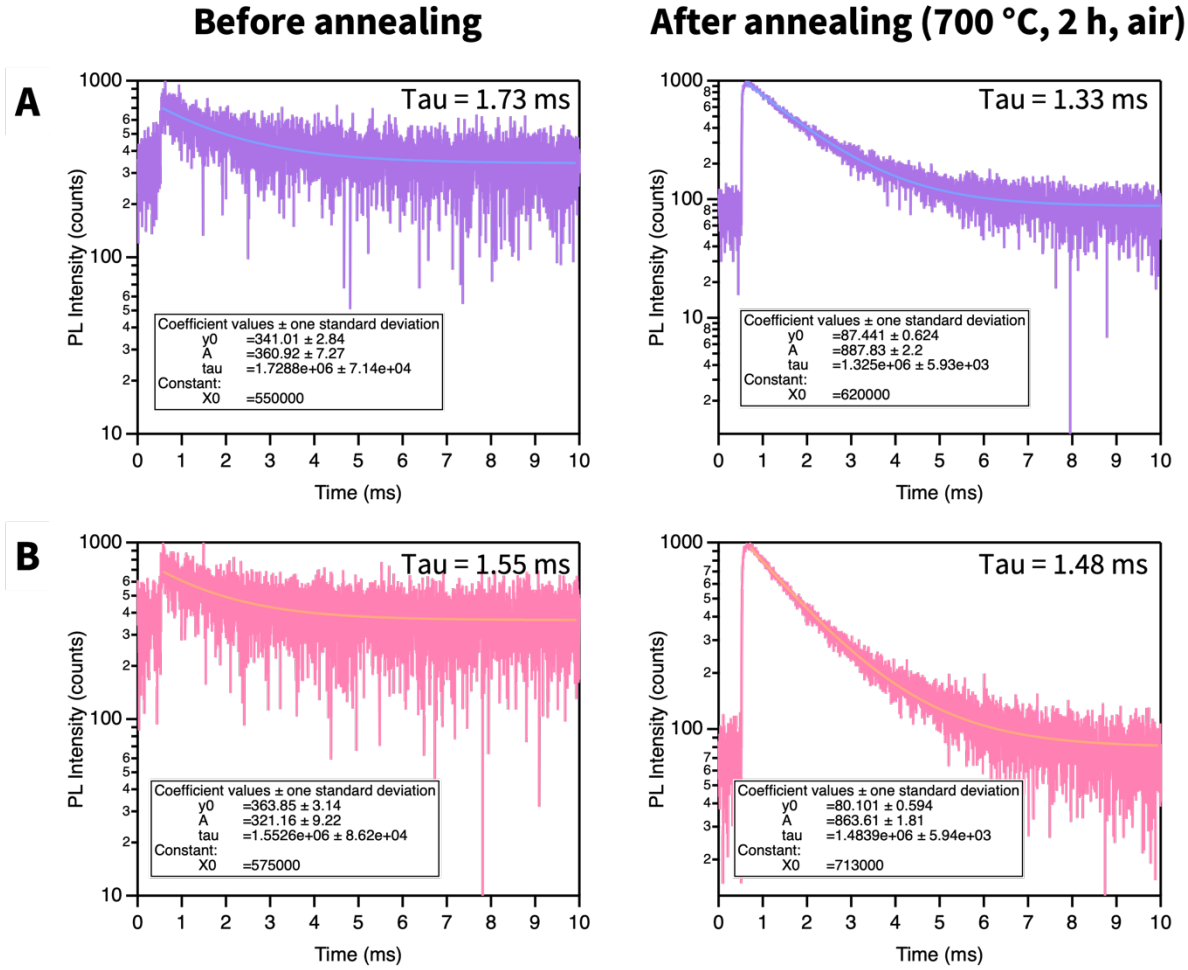


Figure A.5. 1.22% Er^{3+} -doped CeO_2 before and after annealing at 700 °C for 2 h in air across (A) trial 1 and (B) trial 2.

We attempted to synthesize even lower Er^{3+} concentration samples, in which we targeted 0.05% and 0.01% Er, then compared their PL decay by TRPL measurements before and after annealing at 700 °C for 2 h in air (**Figure A.6**). As can be seen in the pre-anneal (pink trace) for 0.05% Er, the PL lifetime appears to improve from 6.1 ms to 21.8 ms, which is a promising result. But, at 0.01% Er, we do not see the same trend. Additionally, measuring the true Er^{3+} concentrations by ICP-OES was challenging due to limitations in our calibration curves and the detector used. In the future, the use of higher-sensitivity ICP-MS for such low concentrations of Er^{3+} is advised. Based on our success with Yb^{3+} -doped CeO_2 measurements before

and after annealing, I am encouraged to believe that, with optimization and sufficient measurement of the Er^{3+} concentration, this trend of annealing significantly improving lifetime may be verified for $\text{CeO}_2:\text{Er}^{3+}$.

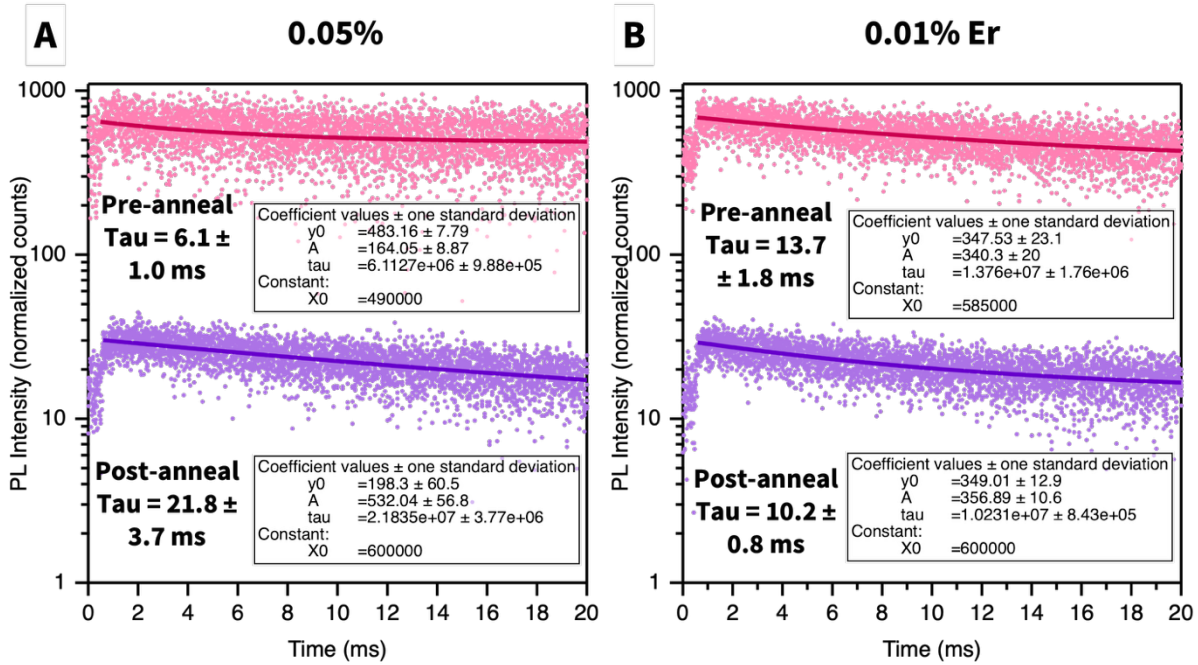


Figure A.6. TRPL data of before and after annealing at 700 °C for 2 h in air with (A) nominal 0.05% Er^{3+} -doped CeO_2 and (B) nominal 0.01% Er^{3+} -doped CeO_2 .

A.2.2. Silica-Shelled Er^{3+} -Doped CeO_2 Nanocrystals

One path towards the isolation of Er^{3+} dopants in CeO_2 hosts is encapsulation within a dense silicon dioxide shell. This method has been used previously to encapsulate quantum dots for single-photon emission by shelling stable quantum dots to increase size without perturbing quantum-confined emission and enhance photostability.⁶ Previous reports have suggested that even at extremely low concentrations (less than one Er^{3+} per nanocrystal), perturbations from the hydrogen nuclei on the surface of the nanocrystals still had deleterious effects on the Er^{3+} spin coherence times.² We performed some preliminary shelling experiments following the previously reported methods⁶ using tetraethyl orthosilicate (TEOS) as our silica precursor to form silica-shelled $\text{CeO}_2:\text{Er}^{3+}$ for improved spin properties. First, to confirm that shelling was possible, we shelled both 0.08% Er and 1.48% Er nanocrystals using stock solutions of cores

prepared at varying concentrations, calculated based on nanocrystal size and thermogravimetric analysis of the approximate ligand content. As seen in **Figure A.7**, we used 10 μL of 0.08% Er^{3+} -doped CeO_2 cores and 20 μL of 1.48% Er^{3+} -doped CeO_2 cores, both yielding ~ 150 nm silica-shelled CeO_2 nanocrystals with approximately one particle per shell (identified by dotted circles).

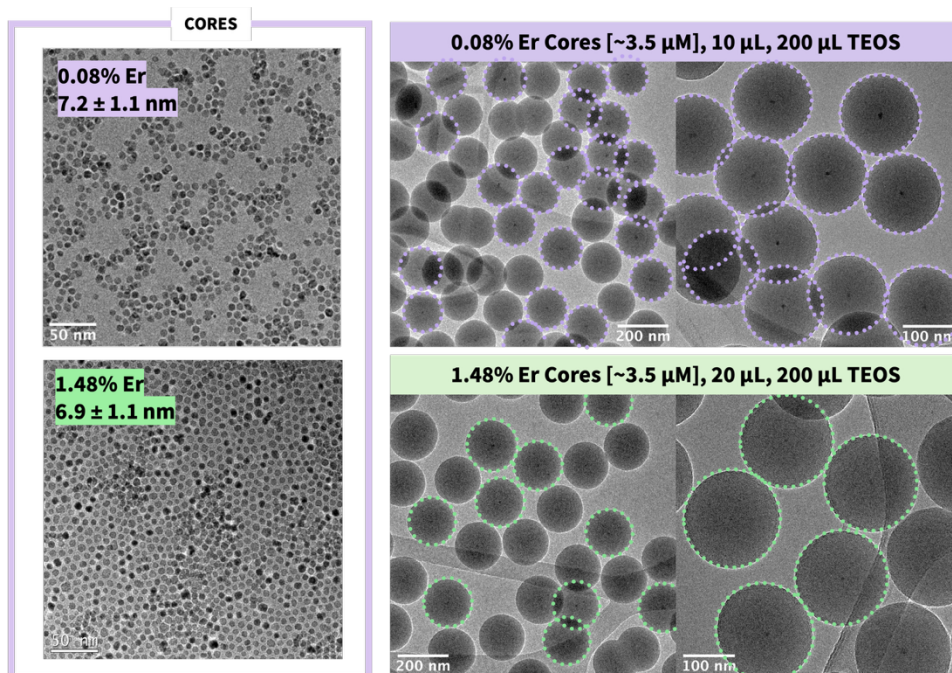


Figure A.7. TEM data of 0.08% Er^{3+} -doped CeO_2 cores and 1.48% Er^{3+} -doped CeO_2 cores used in silica shelling to yield silica-shelled Er^{3+} -doped CeO_2 nanocrystals.

These results were exciting, however measurement of the Er^{3+} by PL and TRPL after shelling was not possible. Our instrument limitations meant that at room temperature, we could only excite between 200–1000 nm, which limited our excitation pathway through CeO_2 sensitized excitation. Silica shelling results in an insoluble white powder that could not be excited at 320 nm as we were able to do with the $\text{CeO}_2:\text{Er}^{3+}$ nanocrystals. Additionally, we did not have access to a room temperature or 4 K set-up for PL or TRPL measurements using direct excitation of Er^{3+} , at 1473 nm.¹

We thus turned to EPR spectroscopy to probe the Er^{3+} spins before and after shelling. We re-prepared even lower concentration silica-shelled $\text{CeO}_2:\text{Er}^{3+}$, with nominal Er^{3+} concentrations of 100 ppm and 500 ppm. **Figure A.8** shows the cores, the ~ 150 nm silica-shelled $\text{CeO}_2:\text{Er}^{3+}$ particles, and the resulting CW

EPR data from the particles before shelling and after shelling. The primary resonance ~ 100 mT is due to the Er^{3+} ($g \sim 6.75$ in literature)^{7,8} with associated low intensity peaks arising from the hyperfine interactions of ^{167}Er ($I = 7/2$). Our main observation from these results was that, after silica shelling, the signal intensity was too weak to accurately measure spin relaxation and coherence lifetimes, given the extremely low yield of shelled particles.

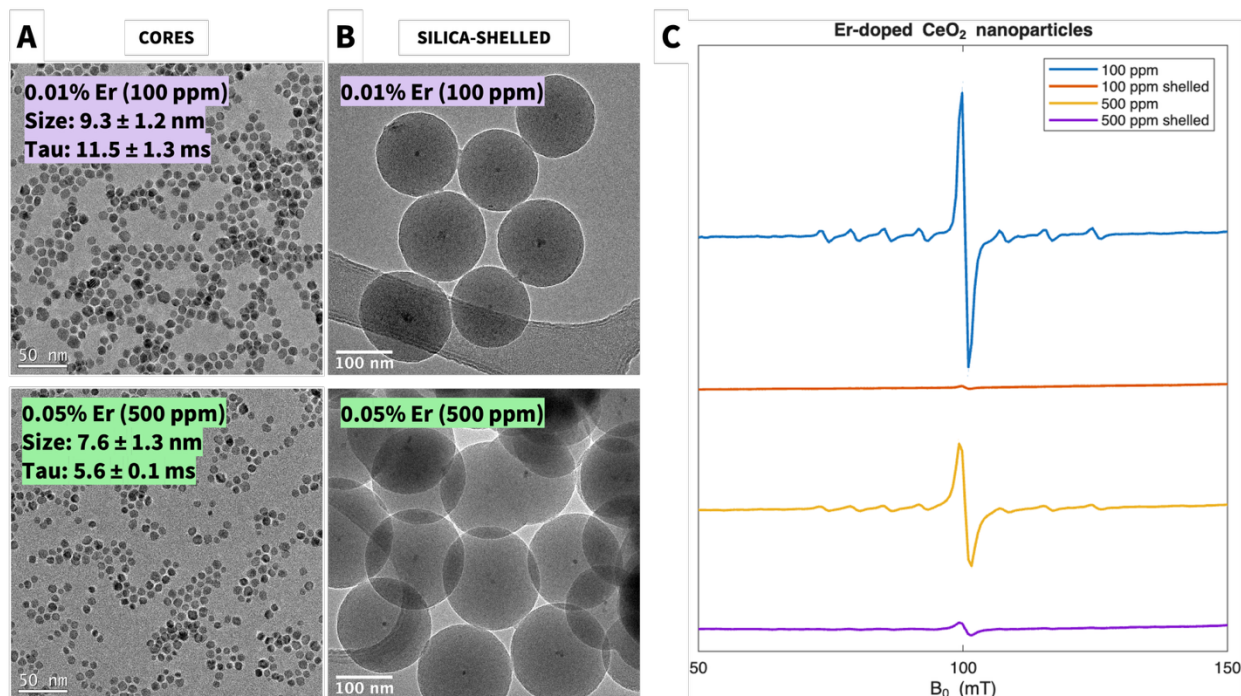


Figure A.8. TEM images of 0.01% and 0.05% Er^{3+} -doped CeO_2 nanocrystal (A) cores, (B) after silica shelling. (C) CW EPR (9.4 GHz, 5 K) spectra of core and silica-shelled $\text{CeO}_2\text{:Er}^{3+}$.

A.2.3. Atomic Layer Deposition to Encapsulate Er^{3+} -Doped CeO_2 Nanocrystals

In another attempt at encapsulation of CeO_2 nanocrystals for better isolation of the Er^{3+} spin defect, we investigated the possible shelling of CeO_2 with CeO_2 or other M^{4+} oxides (ZrO_2 and HfO_2)⁹ via thermal decomposition, and both slow and fast injection of precursors at varying temperatures. The results of these attempts, starting with ~ 7 nm $\text{CeO}_2\text{:Er}^{3+}$ nanocrystal cores, often led to the nucleation of new CeO_2 , ZrO_2 , or HfO_2 nanocrystals, depending on the precursor, suggesting that seeded growth of CeO_2 was less favorable than nucleation in many of the conditions tested. Additionally, attempts to reproduce and continually grow

CeO₂ via previously reported methods¹⁰ were unsuccessful and often yielded much smaller particles than other syntheses. If this synthesis is effectively harnessed for particle sizes of 10+ nm, it would certainly be a promising avenue of research.

We turned to atomic layer deposition (ALD) in collaboration with the **Banerjee** lab at the University of Central Florida as an alternative method of CeO₂ encapsulation, where our preliminary studies started by creating a spin-coated nanocrystal film, followed by ALD with cerium precursor Ce(iPrCp)₂(N-iPr-amd), also known as “celine,” and a co-precursor of H₂O or O₂ plasma, compared to trimethylaluminum (TMA) with H₂O to form an Al₂O₃ coating.¹¹ We prepared a series of samples for each co-precursor condition and investigated the impacts on PL lifetime before and after ALD of celine onto spin-coated ~7 nm 0.33% Er³⁺-doped CeO₂ nanocrystals (**Figure A.9**). I must note that these preliminary experiments were done with CeO₂:Er³⁺ nanocrystals synthesized via a biphasic hydrothermal method (prior to adopting the thermal decomposition methods investigated above) and yielded slightly irregular nanocrystals capped with oleic acid ligands.¹² The lifetimes from these syntheses at similar Er³⁺ concentrations were typically lower than those from the thermal decomposition methods discussed in Section 1.2.1. Each precursor was deposited at a chamber temperature of 245 °C under vacuum, with the exception of the TMA co-precursor, which was deposited with the H₂O co-precursor at a chamber temperature of 200 °C. The celine precursor was heated to 145 °C for a 14 s deposition pulse, and each co-reactant (H₂O and O₂ plasma) was at room temperature when pulsed into the chamber.

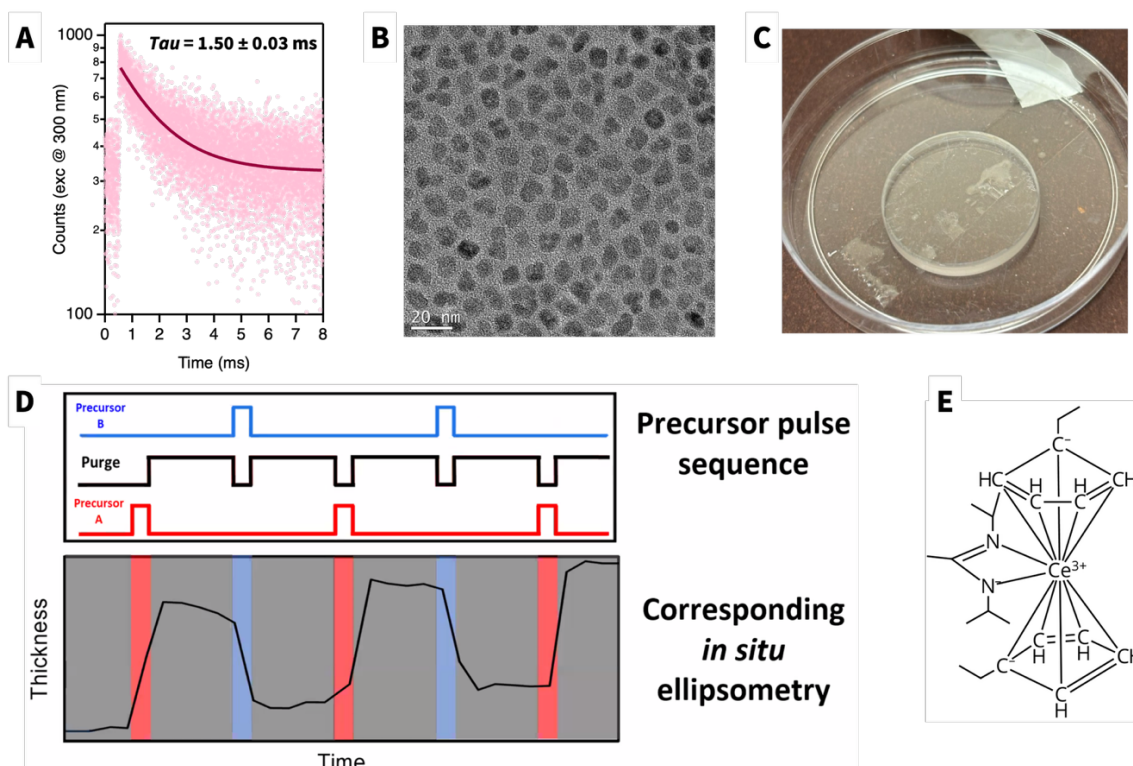
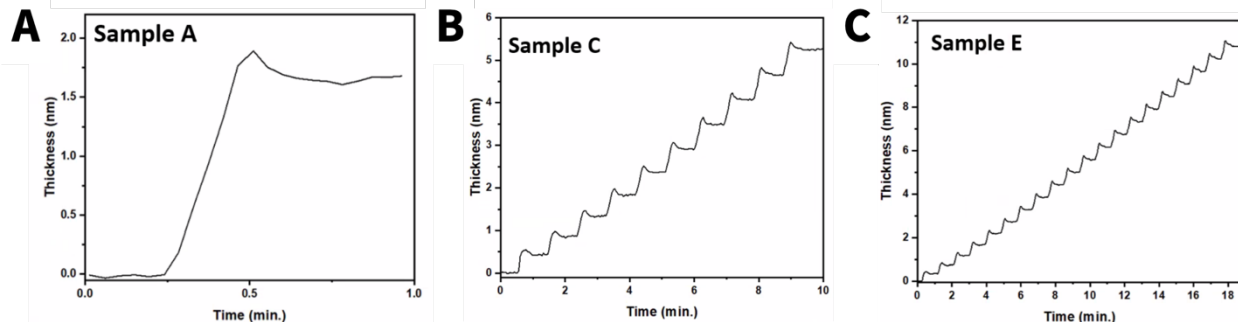


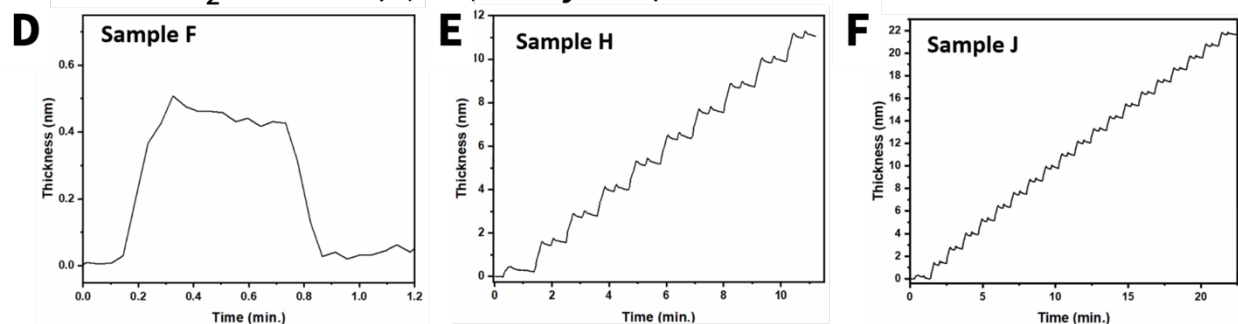
Figure A.9. (A) TRPL data and (B) TEM image of 0.33% Er^{3+} -doped CeO_2 nanocrystals spin-coated on a fused silica disc depicted in (C). The layer of coating is generally too thin to see by eye. (D) Top diagram shows precursor A (celine or TMA) and co-precursor Precursor B (H_2O or O_2 plasma) pulse sequence during ALD process; bottom diagram shows associated *in situ* ellipsometry data measuring cycle-by-cycle thickness growth over time. (E) Cerium ALD precursor $\text{Ce}(\text{iPrCp})_2(\text{N-iPr-amd})$ also called “celine.”

Figure A.10 shows the *in situ* ellipsometry measurements of each set of samples with the associated co-precursor across varying numbers of cycles. In general, it is expected that the co-precursor will cause a decrease in thickness after deposition of precursor A (celine or TMA). The ellipsometry data show that the co-precursor strongly influences the thickness imparted per cycle, with O_2 plasma yielding the thickest deposition (~ 21 nm) after 20 cycles, compared with H_2O and TMA with H_2O . Celine with H_2O co-precursor and TMA with H_2O co-precursor only reached ~ 11 nm and 0.8 nm after 20 cycles, respectively.

Celine & H₂O (1, 10, 20 cycles)



Celine & O₂ Plasma (1, 10, 20 cycles)



TMA & H₂O (1, 10, 20 cycles)

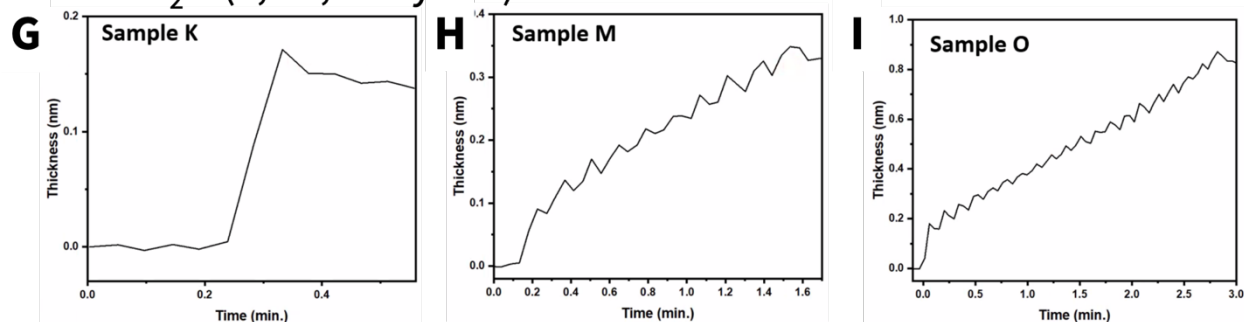
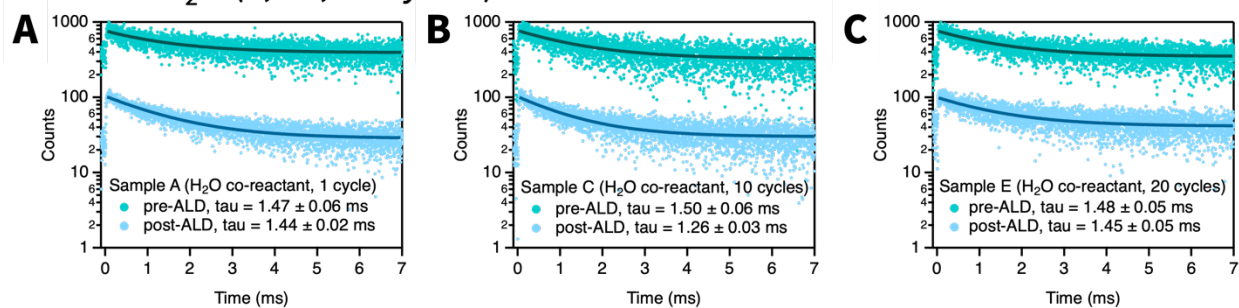
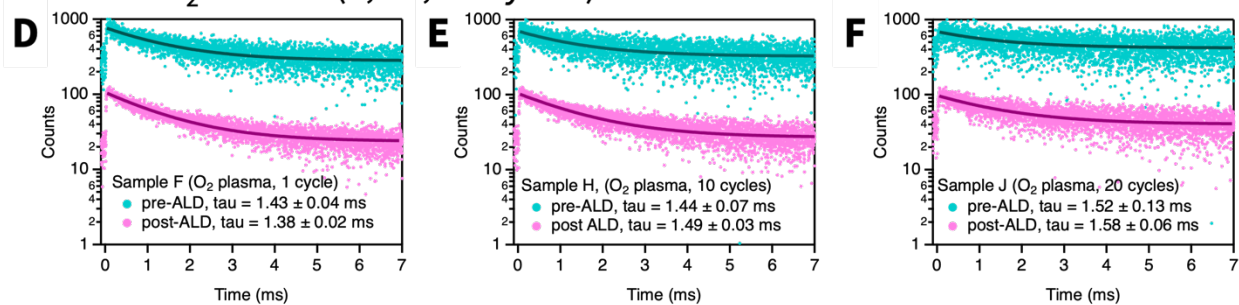


Figure A.10. *In situ* ellipsometry data during ALD of (top row) celine and H₂O co-precursors after (A) 1 cycle, (B) 10 cycles, and (C) 20 cycles, (middle row) celine and O₂ plasma co-precursors after (D) 1 cycle, (E) 10 cycles, and (F) 20 cycles, and (bottom row) TMA and H₂O co-precursors after (G) 1 cycle, (H) 10 cycles, and (I) 20 cycles.

Celine & H₂O (1, 10, 20 cycles)



Celine & O₂ Plasma (1, 10, 20 cycles)



TMA & H₂O (1, 10, 20 cycles)

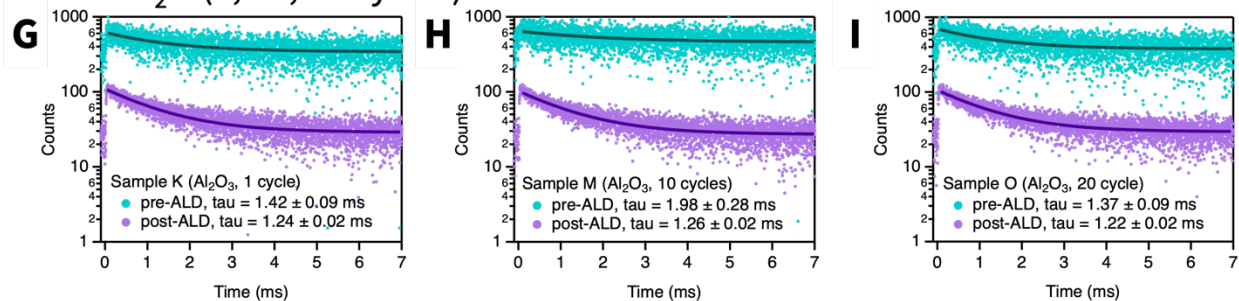


Figure A.11. TRPL data before and after ALD with (top row) celine and H₂O co-precursors after (A) 1 cycle, (B) 10 cycles, and (C) 20 cycles, (middle row) celine and O₂ plasma co-precursors after (D) 1 cycle, (E) 10 cycles, and (F) 20 cycles, and (bottom row) TMA and H₂O co-precursors after (G) 1 cycle, (H) 10 cycles, and (I) 20 cycles.

After taking TRPL measurements of the samples before and after ALD under varying precursor conditions, it is clear that the lifetimes do not change significantly, nor does the signal quality improve (Figure A.11). This could be due to a number of factors: first, the nanocrystal films were prepared via drop-casting oleic acid-capped nanocrystals with no annealing step before ALD. It is possible that the Ce³⁺, oxygen vacancies, and ligands on the surface, as a result of the biphasic hydrothermal synthesis, were

naturally inhibiting Er^{3+} lifetimes regardless of the following ALD step. Second, it is possible that we are in a regime where the Er^{3+} lifetime is limited by Er-Er interactions, nanocrystal heterogeneity, or both. Third, we did not characterize the exact thickness of the $\text{CeO}_2\text{:Er}^{3+}$ thin film that was initially spin-coated on the fused silica discs; it is certainly possible that the ALD of additional CeO_2 (regardless of precursor) will have no measurable effect, given that there is likely significantly more than a monolayer of nanocrystals deposited on the substrate. The spin-coated nanocrystal volume was primarily determined by the amount of sample needed to observe the CeO_2 transition via UV–visible absorption spectroscopy and the Er^{3+} emission via TRPL, typically $\sim 20\text{--}30\ \mu\text{L}$ of concentrated nanocrystal sample dispersed in hexane.

When we look more closely at the exact changes in PL lifetime (graphed as $\Delta\tau$ in **Figure A.12**), however, a few trends emerge. It appears that the Al_2O_3 coating formed from the TMA co-precursor between celine depositions was the least effective in both depositing a film, based on the ellipsometry data, and improving the PL lifetime. The H_2O co-precursor also had no apparent trend on the lifetimes as a function of film thickness, although the formation of the film thickness of CeO_2 was improved over the Al_2O_3 coatings. Curiously, the O_2 plasma as a co-precursor suggests a possible change in the samples as a function of film thickness. We hypothesized that the O_2 plasma potentially has a positive effect on coatings of 10 to 20 cycles, where O_2 could re-oxidize the surfaces of the nanocrystals, thereby reducing defects and improving Er^{3+} PL lifetimes.

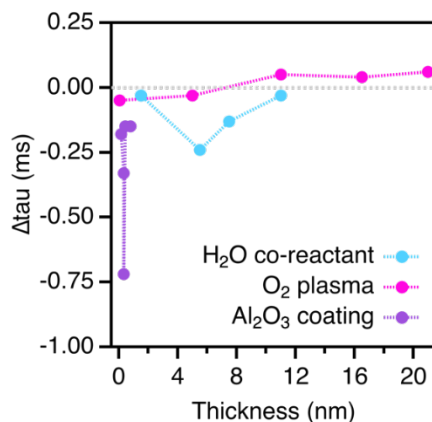


Figure A.12. Change in PL lifetime ($\Delta\tau$) with respect to thickness after 1, 5, 10, 15, and 20 cycles of co-precursors H_2O , O_2 plasma, and TMA.

Our next steps to investigate this approach was doing a sequential comparison of the PL lifetimes of $\text{CeO}_2:\text{Er}^{3+}$ (0.08% Er^{3+}) before annealing, after annealing at 700 °C, which we had identified previously to improve signal-to-noise and lifetime, followed by ALD with celine and O_2 plasma co-precursor at varying cycles. The preliminary results of these steps are shown in **Figure A.13**. The as-synthesized samples are clearly very low in intensity and suffer from poor emission, however the lifetimes of what is emitting is reasonably long and relatively similar to samples we had measured at similar concentrations previously. After annealing, lifetimes of Er^{3+} increase significantly from ~3 ms to ~12 ms on average across three samples, and we again see a rise time in this data as well. The caveat with this preliminary data is that our lifetimes are not accurately measured or fitted, given the abrupt downturn in the data and the fits, suggesting that the lifetimes are longer than the measurement window of 10 ms. If it is similar to the samples in **Figure A.6**, which reported a lifetime increase of ~6 ms to ~22 ms at a nominal doping concentration of 0.05% Er, we can propose that these 0.08% Er samples are likely to increase by ~3–4 orders of magnitude as well, which is similar to what we observe with a shortened window. These samples were then treated with 3, 5, and 10 cycles of celine & O_2 plasma. The lifetimes were measured over a longer window (20 ms), but this window is likely still not long enough to fully resolve the decay of the Er^{3+} emission signal. Despite this, we do see an improvement in lifetimes after 3 and 5 cycles of ALD (corresponding to sample thicknesses of around 3 and 5 nm). It is possible that the 10-cycle sample could continue this trend, but re-measurement would be required to confirm it.

As-synthesized

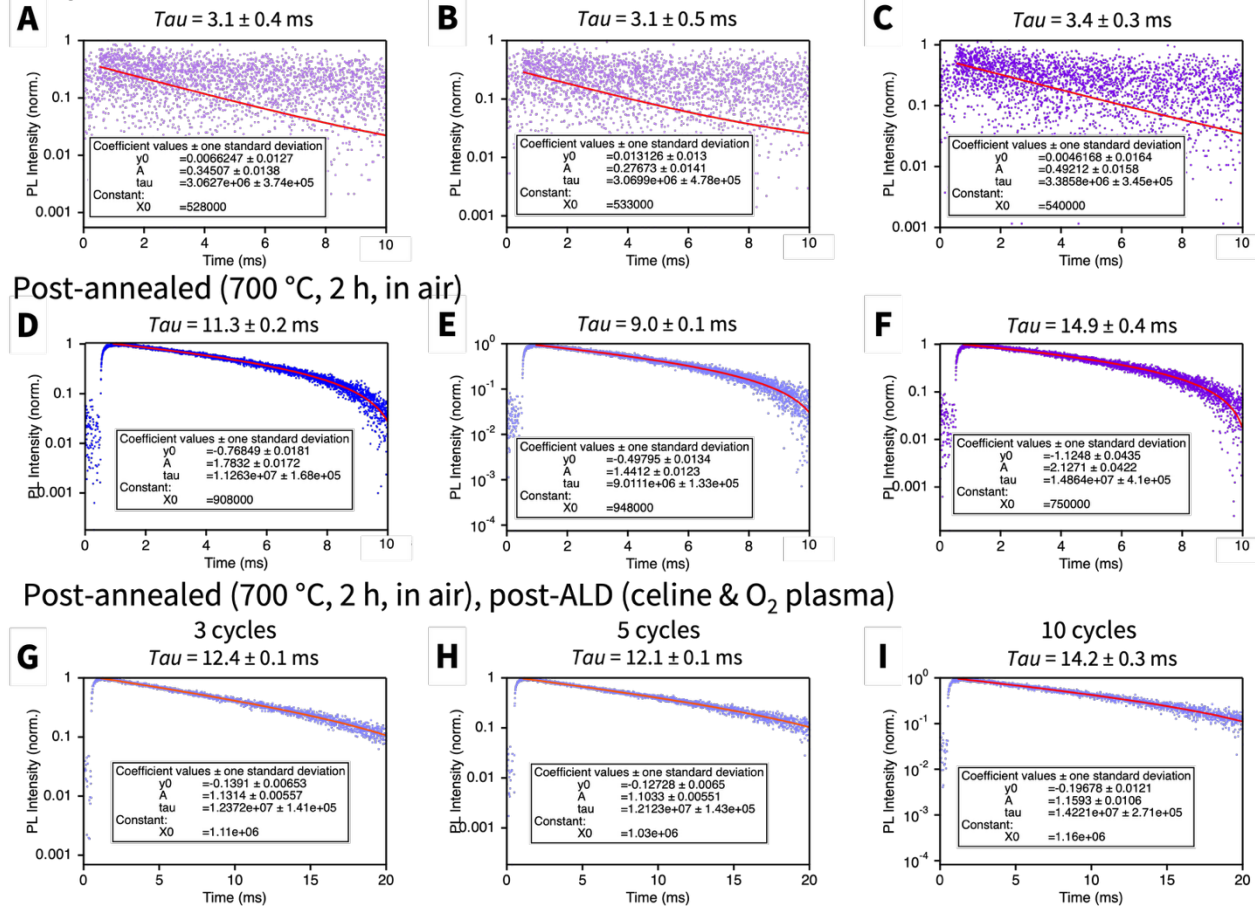


Figure A.13. TRPL data of 0.08% Er^{3+} -doped CeO_2 nanocrystals deposited as spin-coated nanocrystals films on fused silica discs prepared (top row, **A–C**) as-synthesized, followed by (middle row, **D–F**) annealing at 700 °C for 2 h in air, followed by (bottom row) ALD with celine and O_2 plasma co-precursors over (**G**) 3, (**H**) 5, and (**I**) 10 cycles.

A.3. Conclusion

In conclusion, we investigated multiple methods for CeO_2 synthesis and encapsulation to better understand how to improve CeO_2 as a qubit-host lattice. While the nucleation of CeO_2 is well studied, controlling nanocrystal homogeneity and sequential nanocrystal growth remain significant challenges. Additionally, specific placement of the Er^{3+} dopant and control of concentrations down to the single-atom

level have yet to be achieved in concert with these additional encapsulation methods, where their evaluation will be much more meaningful. It should be noted, however, that single-atom Er^{3+} dopants in nanocrystalline CeO_2 have been reported in the literature, validating the feasibility of this strategy.²

Our synthesis investigations demonstrated that changing ligand ratios and controlling additives such as water do impact the quality of the nanocrystals, but further work needs to be performed to accurately produce a correlation between nanocrystal size (monodispersity, morphology, etc.) and Er^{3+} PL lifetimes and spin relaxation and coherence lifetimes at much lower Er^{3+} concentrations (ideally <50 ppm). Furthermore, because annealing a nanocrystal film clearly grows nanocrystal size and hinders colloidal stability, being able to tune the surface defects via *in situ* oxidation, or exploring options for blending nanocrystals with polymer or otherwise inert spacers may be more compelling for their applications broadly.

The silica-shelled nanoparticles are a fascinating proof of concept that, if given enough time to produce enough sample with sufficient signal-to-noise, could be worthwhile to investigate. Assuming the dense silica shells are effective in reducing the hydrogen nuclei spin bath surrounding the nanocrystals, studying their impact (either by toggling Er^{3+} concentrations <50 ppm or by toggling silica shell size itself) could produce valuable insights on the capability of Er^{3+} encapsulation via nanoscale heterostructures. An interesting question would also be whether the $\text{CeO}_2/\text{SiO}_2$ core/shell interface with enhance or mitigate CeO_2 surface defects such as oxygen vacancies and Ce^{3+} .

Finally, the ALD approach to CeO_2 encapsulation is promising, but it is possible that the initial approach we took was conceptually flawed in one major aspect: the nanocrystal thin film is not properly encapsulated when it is deposited first—the following ALD layers are effectively only embedding the Er^{3+} dopant from one side, which is insufficient for full encapsulation. Another method might be adding an Er^{3+} precursor or a mixture of $\text{Er}^{3+}/\text{Ce}^{3+}$ (where Er^{3+} concentration <50 ppm) and depositing a film where the dopant may be dispersed throughout a perfectly crystalline CeO_2 matrix. In this case, studies using epitaxy have already demonstrated such approaches, and to much lower Er^{3+} concentrations and higher crystallinity already.^{1,4,3} A future study of this system may perhaps be conducted by taking much larger (defect-free, ideally) $\text{CeO}_2:\text{Er}^{3+}$ nanocrystals, and disperse individual particles randomly between multiple ALD layers of CeO_2 ,

thereby imparting both a Er^{3+} concentration dependence (finely tuned by the CeO_2 nanocrystal synthesis) and Er^{3+} dopant positioning within a bulk CeO_2 lattice. This study could be actualized by using varying low Er^{3+} concentration nanocrystals (ideally 50+ nm with Er^{3+} at <50 ppm) and varying the concentration of their addition to the deposition process (i.e. more or less nanocrystals evenly dispersed in between ALD layering steps as a means of controlling Er^{3+} placement or Er-Er distances). Annealing these samples (at temperatures even higher than 700 °C) after ALD to heal defects in the lattice after deposition may also be a method to improve the crystallinity the entire system. Finally, studying the varying films for spin relaxation and coherence properties would allow us to benchmark this study with respect to the prior nanocrystal and epitaxially-grown $\text{CeO}_2\text{:Er}^{3+}$.

A.4. Experimental Methods

A.4.1. General Methods and Materials

All synthetic preparations were performed in ambient air in a well-ventilated fumehood or on a benchtop unless otherwise stated. All chemicals listed below were used without further purification unless stated otherwise. Cerium(III) nitrate hexahydrate ($\geq 99\%$ trace metals basis), erbium(III) nitrate pentahydrate ($\geq 99.9\%$ trace metals basis), oleylamine (technical grade, 70%), octadecylamine, 1-octadecene (technical grade, 90%), toluene (ACS reagent, $\geq 99.5\%$), hexanes (ReagentPlus, $\geq 99\%$), methanol (ReagentPlus, $\geq 99\%$), acetone (ACS reagent, $\geq 99.9\%$), cyclohexane, hexanol, tetraethyl orthosilicate (TEOS, 99.999%), Triton X-100, ammonium hydroxide solution (NH_4OH , 28.0–30.0% w/w) were all purchased from Millipore Sigma.

A.4.2. Synthesis of $\text{CeO}_2\text{:Er}^{3+}$ Nanocrystals via Thermal Decomposition

As described by Lee et al.,⁵ cerium(III) nitrate hexahydrate ($1-x$ mmol) and erbium(III) nitrate pentahydrate (x mmol, $x = 0.001-1$) were added to a 50 mL 3-neck round bottom flask equipped with a condenser, thermal probe, and stir bar. For the 0.005 and 0.001 mmol quantities, a stock solution of erbium(III) nitrate pentahydrate was dissolved in a known volume of methanol, which was then transferred as a μL volume to the reaction flask according to the desired ytterbium concentration. Oleylamine (0.98 mL, 3 mmol) or a mixture of oleylamine and octadecylamine (1.5 eq. each) and 1-octadecene (4 g, 5.07 mL) were added to the mixture, forming a clear solution. In syntheses using water, 4 eq. of distilled H_2O were also added. The mixture was heated to 80 °C while stirring, turning into a clear yellow solution, and held at 80 °C for 30 minutes. Then, the temperature was quickly ramped to 260 °C and held for 2 hours, turning into a dark brown solution, then cooled to room temperature. The reaction mixture was purified by a series of centrifugation steps. First, the crude reaction mixture was transferred to a Falcon tube and precipitated using ~ 30 mL of acetone, followed by centrifugation at 8000 rpm for 10 min. The supernatant (typically a clear light brown on the first crash out) was poured off and the pellet was redissolved in hexanes. The solution was crashed out twice more with additional acetone. The final pellet was redissolved in hexanes. The particle solution in hexanes is used for TEM sample preparation, XPS sample preparation, XRD sample preparation, and PL/PLE/TRPL sample preparation.

A.4.3. Silica Shelling of $\text{CeO}_2\text{:Er}^{3+}$ Nanocrystals

Following previously reported methods by Nguyen et al.,⁶ to a mixture of 10 mL cyclohexane, 1.9 mL of Triton X-100, 1.8 mL of hexanol, 10–20 μL of a concentrated solution of $\text{CeO}_2\text{:Er}^{3+}$ nanocrystals in hexanes were added. The mixture was stirred for 30 min, followed by dropwise addition of 200 μL of TEOS and stirred for another 15 min. Finally, 30 μL of ammonium hydroxide solution and 0.2 mL of distilled water were injected successively. The reaction was stirred in the dark. After 2–3 days, a 1:1 ratio solution of acetone and ethanol (20 mL) was added to the solution followed by 5 min centrifugation at 5000 rpm.

The white precipitate was collected and washed with ethanol three times. The final product was stored as a dry powder in air at room temperature.

A.4.4. Instrumentation and Characterization Methods

Transmission electron microscopy (TEM) images were obtained with a FEI Tecnai G2 F20 SuperTwin microscope operated at 200 kV using bright field imaging. All samples were prepared by drop-casting 5 μ L of sample dissolved in hexanes onto a suspended ultrathin carbon film on lacey carbon support film, 400 mesh, copper grids purchased from Ted Pella, Inc. The samples were allowed to dry in air for 5 min until the hexanes evaporated. All grids were placed under vacuum overnight to ensure complete dryness before imaging.

Elemental analysis was performed by inductively coupled plasma-optical emission spectroscopy (ICP–OES) on a Perkin Elmer Optima 3000. Samples were digested for 48 h in a 1:1 conc. $\text{H}_2\text{O}_2/\text{HNO}_3$ (concentrated) then filtered through a PTFE filter and diluted to 2% HNO_3 for analysis.

Annealing was performed in a quartz tube using a Lindberg/Blue M Mini-Mite Tube Furnace with ambient air flow. The temperature was raised to either 500 °C or 700 °C at a rate of 10 °C/min and kept at 500 °C or 700 °C for 2 h.

Room temperature photoluminescence (PL), photoluminescence excitation (PLE), and time-resolved photoluminescence (TRPL) measurements were collected on an Edinburgh FLS1000 photoluminescence spectrometer equipped with a 450 W ozone-free Xenon arc lamp, a microsecond Xenon flashlamp, and an NIR PMT (PMT-1700). PL, PLE, and TRPL data were collected using samples either as dilute colloidal stable samples suspended in hexanes or as solid state samples drop-cast onto fused silica substrates. For erbium measurement specifically, an excitation wavelength of 320 nm and an emission wavelength of 1530 nm was used. Bandwidth windows of 5–10 nm were used for both excitation and emission depending on the signal. For TRPL, a pulse range for a 10–20 ms scale with 2000 channels was typically used.

Continuous-wave X-band (CW) electron paramagnetic resonance (EPR) spectra at 9.4 GHz and 5 K were collected on a Bruker EMX spectrometer equipped with a Bruker SHQE resonator and an Oxford

Instruments ESR900 cryostat. Pulse X-band EPR experiments were performed at 9.7 GHz and 4 K on a Bruker ElexSys E580 spectrometer equipped with a 1 kW amplifier, a Bruker MD4 resonator, and an Oxford Instruments CF9350 cryostat. For both CW and pulse experiments the cryostats were cooled with liquid helium and the temperature was set with an Oxford Instruments ITC503 temperature controller.

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VITA

Emily grew up in Tucson, Arizona before departing the southwest to move across the country and attend Barnard College of Columbia University in New York City, NY. While at Barnard, she performed undergraduate research with Professor Michael G. Campbell synthesizing inorganic molecular complexes to investigate photoredox properties from the summer of 2018 to the summer of 2021. She graduated with her B.A. in Chemistry in 2021, after which she moved across the country (again!) to Seattle, WA to pursue a Ph.D. in Chemistry at the University of Washington (UW). In January of 2022, she joined the lab of Professor Brandi M. Cossairt, where she explored the synthesis and characterization of metal oxide nanomaterials, mostly cerium oxide (with a few other oxides here and there). From 2025–2026, she took a seven-month long hiatus from her graduate studies to do an internship at Applied Materials in Gloucester, MA. During her research career, she has published two first-author papers focused on the defect engineering of cerium oxide for catalysis and quantum bit applications and supported fellow Cossairt lab mates on a handful of other publications.

Outside of the lab, she was also an active member of the UW Chemistry Department, committed to science outreach and community. She served as the president of the Inclusion in Chemical Sciences (InCS) club from 2023–2025 hosting several talks, events, and panels for the chemistry graduate students, and collaborated with her lab mate Dr. Hao Nguyen to run the Summer Chemistry Research Opportunity for Community College Students (SCROCCS) from 2023–2025 before passing both projects onto the next generation of graduate students. She has also participated in extensive outreach projects as an Education and Training Fellow with the UW Molecular Engineering Materials Center, helping to design K-12 outreach programs, summer research program lesson plans, and even traveling to Honolulu, Hawaii to teach a nanomaterials outreach lessons to local middle and high school students. In her free time, she enjoys cooking/baking, reading, hanging out with (bothering) her two cats (Goose and Puffin), and spending the occasional sunny day outdoors.