

Article

Tuning Oxygen Vacancies and Microstrain in CeO₂ Nanoparticles: A Raman-Based Synthesis–Property Map for Rare-Earth Catalysis

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Abstract

Cerium oxide (CeO₂) is a key rare-earth material for catalysis and energy applications, yet quantitative links between synthesis parameters, morphology, and defect chemistry remain scarce. Using three selected conditions from a broader synthesis matrix with octadecylamine (ODA) concentration (0.01–0.2 M) and ethanol/water ratio ($\alpha = 0.3$ –3.0), we obtained three distinct morphologies: spherulites (CeO₂-AA), short nanorods (CeO₂-BB), and long rods (CeO₂-MM). CeO₂-BB nanorods exhibit the highest BET surface area (79.9 m²/g), Ce³⁺ content (30.2%), and $O_{\text{def}}/O_{\text{lat}}$ ratio (0.99), while CeO₂-MM shows an $O_{\text{def}}/O_{\text{lat}}$ ratio of 0.80. A controlled comparison with commercial 25 nm CeO₂ (similar crystallite size, 21.3 nm, but 60× lower microstrain) reveals that, within the investigated sample set, microstrain and defect-related disorder are the dominant contributors to Raman F_{2g} broadening, rather than phonon confinement. The I_D/I_{F2g} ratio correlates strongly with Ce³⁺ content ($R^2 = 0.94$), supporting Raman as a sensitive indicator of defect-related disorder or oxygen-vacancy-associated defects. Qualitative inspection of the data suggests that ODA concentration has a more pronounced influence on aspect ratio, Ce³⁺ content, and bandgap than the ethanol/water ratio, although the limited number of synthesis conditions precludes definitive statistical ranking. This integrated framework enables rational design of CeO₂ nanostructures with tailored defect chemistry for catalysis and rare-earth-based applications.

Keywords: cerium oxide; ceria nanostructures; morphology control; oxygen vacancies; Raman microstrain; structure–property relationships



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1. Introduction

Cerium oxide (CeO₂, ceria) is a versatile functional material central to heterogeneous catalysis [1,2], energy storage/conversion [3,4], biomedicine [5,6], and environmental remediation [7,8]. Its technological importance stems from the reversible Ce³⁺/Ce⁴⁺ redox couple, high oxygen storage capacity, ability to form/annihilate oxygen vacancies without structural collapse, and tunable electronic structure [9,10]. The oxygen vacancies in CeO₂ play a crucial role in its catalytic performance. For instance, ceria-supported Ru⁰-Ru⁺ clusters have been shown to be efficient catalysts for arene hydrogenation [11], and CeO₂ nanostructure/carbon composites have demonstrated enhanced performance

in wastewater treatment [12]. The concentration and distribution of oxygen vacancies directly influence the redox properties of ceria, which are central to its activity in oxidation reactions, oxygen storage, and photocatalysis. Consequently, CeO₂ is indispensable in three-way catalysts [13], fuel cell electrolytes [14], oxygen sensors [15], and noble metal supports [16,17].

At the nanoscale, CeO₂ properties diverge significantly from the bulk [18,19]. Beyond size effects, morphology governs surface energies and reactivities because different crystal facets are exposed [20–23]. Anisotropic shapes expose specific facets preferentially, leading to facet-dependent catalytic activity [24,25]. For instance, CeO₂ nanocubes (100-rich) show superior oxygen storage capacity over nanorods (110/100-rich) and octahedra (111-rich) [26–28], whereas nanorods exhibit enhanced CO oxidation due to higher surface Ce³⁺ [25].

Despite extensive research, systematic studies linking synthesis parameters to morphology and properties are scarce. Most reports rely on qualitative trends or single-parameter variations [29,30]. Factorial designs that identify dominant parameters and enable quantitative property prediction are rare in the context of CeO₂ morphology control [31–33], although more recent studies have applied similar statistical approaches to optimize other ceria-based materials [34]. Moreover, Raman interpretation remains contentious: phonon confinement is widely invoked to explain F_{2g} broadening [35,36], but recent evidence suggests that microstrain and defect-induced effects dominate in defective samples [37–39]. Disentangling size from strain requires controlled comparisons of similar-sized particles with different microstructural quality—such comparisons are rarely reported.

Here, we selected three conditions from a 3² synthesis matrix varying ODA concentration and ethanol/water ratio to produce three distinct CeO₂ morphologies: spherulites, short nanorods, and long rods. A suite of complementary characterization and data analysis techniques is integrated to establish quantitative synthesis–property relationships: X-ray diffraction (XRD) with Rietveld/FullProf refinement, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), Brunauer–Emmett–Teller (BET) surface area analysis, UV–visible diffuse reflectance spectroscopy (UV-Vis DRS), Fourier-transform infrared spectroscopy (FT-IR), principal component analysis (PCA), and statistical modeling. Two commercial references (25 nm and 5 μm) serve as benchmarks. While ODA-mediated synthesis of CeO₂ nanorods and the effect of ethanol/water ratio on morphology have been previously reported [30,31], the quantitative link between synthesis parameters, microstrain, and oxygen-vacancy-related defect chemistry has not been systematically established. This work addresses this gap by: (i) using a controlled comparison of similar-sized particles with vastly different microstructural quality to disentangle the effects of crystallite size and microstrain on Raman F_{2g} broadening; (ii) establishing quantitative correlations between synthesis parameters (ODA concentration and ethanol/water ratio) and defect-related properties (Ce³⁺ content, O_{def}/O_{lat} ratio, and bandgap); and (iii) proposing the Urbach energy as a more robust descriptor of structural disorder than simple linear models based on Ce³⁺ and microstrain alone. A key finding is that, within the investigated sample set, microstrain and defect-related disorder are the dominant contributors to Raman F_{2g} broadening, rather than phonon confinement. These findings provide a quantitative framework for designing CeO₂ nanostructures with tailored defect chemistry for catalysis and energy applications.

2. Materials and Methods

All reagents were purchased from commercial suppliers (Sigma-Aldrich, St. Louis, MO, USA; J.T. Baker, Phillipsburg, NJ, USA) and used as received. Cerium (III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O, 99.0%, Sigma-Aldrich), octadecylamine (ODA, 97%, Sigma-Aldrich), sodium hydroxide (NaOH, 98%, J.T. Baker), absolute ethanol (99.9%, J.T. Baker),

and deionized water (18.2 M Ω -cm) were used without further purification. Commercial CeO₂ references (25 nm and 5 μ m, Sigma-Aldrich) were used for comparison.

2.1. Synthesis of CeO₂ Nanostructures

CeO₂ nanostructures were synthesized via a surfactant-mediated solvothermal method adapted from previously reported procedures [30,31]. A 3² synthesis matrix was designed with octadecylamine (ODA) concentration (0.01, 0.05, and 0.2 M) and ethanol/water volume ratio (α = 0.3, 1.0, and 3.0) as the two factors. The nine experimental conditions are summarized in Table S1 (Supporting Information). From this matrix, three representative conditions were selected for detailed characterization because they bracket the extreme morphologies: CeO₂-AA (spherulites, high ODA/high EtOH), CeO₂-BB (short nanorods, intermediate ODA/intermediate EtOH), and CeO₂-MM (long nanorods, low ODA/low EtOH).

The selection of ODA concentration and ethanol/water ratio as the two factors was based on their well-documented influence on CeO₂ morphology [30,31]. ODA acts as a structure-directing agent by preferentially adsorbing on specific crystal facets, while the ethanol/water ratio controls the dielectric constant of the solvent, which in turn affects the hydrolysis and condensation kinetics of cerium precursors. Other parameters (temperature, time, pH) were fixed based on preliminary optimization experiments and previous reports [30,31] to isolate the effects of the two main factors.

In a typical synthesis, Ce(NO₃)₃·6H₂O (2.17 g, 5 mmol) was dissolved in a mixture of ethanol and water (total volume 50 mL) at the specified α ratio. ODA was added at the desired concentration, and the mixture was stirred at 60 °C for 30 min to ensure complete dissolution. NaOH solution (1 M, 15 mL, corresponding to a Ce:OH molar ratio of 1:3) was added dropwise under vigorous stirring (500 rpm) over 10 min. The Ce:ODA molar ratio of 1:3 was selected based on preliminary optimization experiments and previous reports [30,31], which demonstrated that this ratio ensures complete cerium complexation and precipitation while avoiding excessive surfactant that would hinder hydrothermal crystallization. At Ce:ODA ratios below 1:2, incomplete precipitation led to isolated product yields below 60%, while ratios above 1:4 did not further improve morphological control and introduced unnecessary organic waste that required more extensive washing and calcination. The pH of the precursor suspension was measured before and after the addition of NaOH using a calibrated pH meter. The final pH varied systematically with the synthesis conditions: pH values ranged from 11.8 $\pm$ 0.1 (high EtOH, low ODA) to 13.2 $\pm$ 0.1 (low EtOH, high ODA), as detailed in Table S1. This variation arises from the combined effects of ODA hydrolysis (which raises pH through amine protonation) and the ethanol/water ratio (which affects the dielectric constant and thus the dissociation of Ce(OH)₃). Higher ODA concentrations and lower EtOH fractions yielded systematically higher pH values.

The resulting suspension was transferred to a Teflon-lined stainless-steel autoclave (100 mL capacity) and heated at 180 °C for 24 h without stirring. After cooling to room temperature, the suspension was aged for 30 min, then the precipitate was collected by centrifugation (8000 rpm, 10 min), washed three times with 30 mL of ethanol/water (1:1 *v/v*), and dried at 80 °C for 12 h in air. The dried powder was calcined at 500 °C for 2 h (heating rate 5 °C/min) in air using a muffle furnace with a sample loading of approximately 0.5 g in an alumina crucible, to remove residual organics and crystallize the CeO₂ phase. The typical cerium-based yield was approximately 85%.

Three representative conditions were selected for detailed characterization: CeO₂-AA (spherulites): 0.2 M ODA, α = 3.0; CeO₂-BB (short nanorods): 0.05 M ODA, α = 1.0; and CeO₂-MM (long rods): 0.01 M ODA, α = 0.3. Each synthesis was performed in triplicate to

assess reproducibility. The intermediate synthesis conditions yielded mixed or transitional morphologies that fall between these three archetypes. By focusing on these morphological extremes, we establish a clear synthesis–property map that brackets the range of achievable structures. The synthesis parameters and the correspondence between expected and observed morphologies are summarized in Table S1.

2.2. Characterization

Powder samples were loaded onto a flat zero-background silicon holder. XRD patterns were collected on a Panalytical X'Pert PRO diffractometer (Malvern Panalytical, Almelo, The Netherlands) with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) in the 2θ range of $20\text{--}80^\circ$, step size 0.02° , counting time 2 s per step. The instrumental resolution function was determined using a well-crystallized CeO₂ reference (5 μm , Sigma-Aldrich, St. Louis, MO, USA) with negligible microstrain, measured under identical conditions and fitted with a pseudo-Voigt function. Rietveld refinement was performed using the FullProf Suite software (version 2019, Institut Laue-Langevin, Grenoble, France) [40] with the fluorite structure (space group Fm $\bar{3}m$, ICSD #28,753) as the starting model. The crystallite size (D) and microstrain (ϵ) were extracted from the refined profile parameters using the integral breadth method (double-Voigt approach). The dislocation density (ρ) was calculated using the formula: $\rho = (2\sqrt{3}\cdot\epsilon)/(b\cdot D)$, where b is the magnitude of the Burgers vector. For CeO₂ with a fluorite structure, the dominant dislocation type is $a/2\langle 110 \rangle$ on $\{100\}$ planes, yielding $b = a\sqrt{2}/2 \approx 3.83 \text{ \AA}$ (where $a = 5.411 \text{ \AA}$ is the lattice parameter) [41,42]. This expression assumes a homogeneous isotropic distribution of dislocations and is commonly used in Williamson–Smallman-type analyses [41,43].

Raman spectra were acquired using a Thermo Scientific DXR3 SmartRaman spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) equipped with a 532 nm laser (5 mW), 2 cm^{-1} resolution, 30 s acquisition time, and 10 accumulations. Spectra were collected in the range of $200\text{--}800 \text{ cm}^{-1}$. Spectral deconvolution was performed using pseudo-Voigt functions (weighted sums of Lorentzian and Gaussian profiles) in the OriginPro 2021 software (OriginLab, Northampton, MA, USA). The F_{2g} mode ($\sim 465 \text{ cm}^{-1}$) and defect-induced D band ($\sim 590 \text{ cm}^{-1}$) were fitted with constraints on the peak positions ($\pm 5 \text{ cm}^{-1}$) and full width at half maximum (FWHM, $5\text{--}50 \text{ cm}^{-1}$). The D band is attributed to oxygen vacancies [44,45].

XPS analysis was performed using a SPECS system (SPECS GmbH, Berlin, Germany) equipped with a PHOIBOS 150 hemispherical analyzer (SPECS Surface Nano Analysis GmbH, Berlin, Germany) and a monochromatic Al K α X-ray source (1486.6 eV, 300 W). Survey spectra (0–1350 eV) and high-resolution Ce 3d, O 1s, and C 1s spectra were acquired with pass energies of 200 eV and 50 eV, respectively. Spectra were calibrated to the adventitious C 1s peak at 284.8 eV. Ce³⁺ quantification was performed using the method described by Burroughs et al. [46], which deconvolutes the Ce 3d spectrum into 10 peaks (6 for Ce⁴⁺: $u, u'', u''', v, v'', v'''$; 4 for Ce³⁺: u, u', v, v'). The Ce³⁺ fraction was calculated as $\text{Ce}^{3+}/(\text{Ce}^{3+} + \text{Ce}^{4+}) = [A(u) + A(u') + A(v) + A(v')]/[\text{total area of all Ce 3d peaks}]$, after Shirley background subtraction and Gaussian-Lorentzian (70:30) fitting. The O 1s spectra were deconvoluted into three components corresponding to lattice oxygen (O_{lat} , $\sim 529.3 \text{ eV}$), oxygen vacancies/defective oxygen (O_{def} , $\sim 531.5 \text{ eV}$), and adsorbed oxygen species (O_{ads} , $\sim 532.8 \text{ eV}$), following established assignments [47].

Bright-field TEM images were acquired using a JEOL JEM-2200FS microscope (JEOL Ltd., Tokyo, Japan) operated at 200 kV, with a Cs corrector, in STEM mode. Samples were dispersed in ethanol by ultrasonication and drop-cast onto lacy carbon-coated copper grids (Ted Pella, Redding, CA, USA). Particle size distributions were determined by measuring 200–300 particles per sample using the ImageJ software (version 1.52k, National Institutes

of Health, Bethesda, MD, USA). The width (W) and length (L) of individual particles were recorded; for spherulites ($\text{CeO}_2\text{-AA}$) the “diameter” was taken as the average of two perpendicular Feret diameters. The aspect ratio (AR) was calculated as L/W .

N_2 adsorption–desorption isotherms were measured at 77 K using an Autosorb[®] iQ analyzer (Quantachrome Instruments, Boynton Beach, FL, USA). Prior to measurement, samples were degassed at 200 °C for 4 h under vacuum ($<10\text{ }\mu\text{m Hg}$). Isotherms were collected over a relative pressure range $P/P_0 = 0.01\text{--}0.99$ using high-purity N_2 (99.99%). The BET surface area was calculated from the linear region of the BET plot ($0.05 < P/P_0 < 0.30$). The total pore volume was determined at $P/P_0 = 0.99$. Pore size distributions were calculated using the Barrett–Joyner–Halenda (BJH) method applied to the desorption branch [48,49]. Micropore analysis was performed using the t-plot method with the Harkins–Jura thickness equation [50] and the Dubinin–Radushkevich (DR) equation [51].

Diffuse reflectance spectra were recorded on a Cary 100 spectrophotometer (Agilent Technologies, Santa Clara, CA, USA) equipped with a Labsphere DRA-CA-30 integrating sphere (Labsphere, North Sutton, NH, USA) over the range of 200–800 nm. Spectralon[®] (Labsphere, North Sutton, NH, USA) was used as the reflectance standard. Reflectance data were converted to absorption using the Kubelka–Munk function: $F(R) = (1 - R)^2 / (2R)$, where R is the reflectance. Optical bandgaps (E_g) were determined from Tauc plots for both direct and indirect allowed transitions: $[F(R) \cdot h\nu]^{1/2}$ for direct and $F(R) \cdot h\nu^2$ for indirect transitions, as a function of photon energy $h\nu$ [52]. Linear regression was performed using weighted least squares with sliding window R^2 -maximization. Urbach energies (E_u) were extracted from the exponential absorption tail below the bandgap by fitting $\ln[F(R)]$ vs. $h\nu$ to the Urbach relation, $F(R) = F_0 \exp[(h\nu - E_0)/E_u]$, where E_0 is the reference energy [53].

FT-IR spectra were recorded using a PerkinElmer Spectrum 100 spectrometer (PerkinElmer, Waltham, MA, USA) equipped with an attenuated total reflectance (ATR) module featuring a diamond crystal. Spectra were collected in the range of 650–4000 cm^{-1} at a resolution of 4 cm^{-1} , with 32 scans. A linear baseline correction was applied to each spectrum. All spectra were then normalized to the total integrated area between 650 and 4000 cm^{-1} . This normalization corrects for variations in sample thickness and crystal contact, which are the dominant sources of non-chemical variability in ATR measurements of loose powders, and provides a consistent basis for comparing relative spectral profiles among samples. Because no invariant internal reference band is available in this system, the normalized values are interpreted as relative rather than absolute surface concentrations. Five spectral regions were analyzed: O–H stretching (3000–3700 cm^{-1}), H–O–H bending (1600–1650 cm^{-1}), C–H stretching (2800–3000 cm^{-1}), high-wavenumber carbonates (1500–1550 cm^{-1} , ν_3 asymmetric), and low-wavenumber carbonates (1350–1450 cm^{-1} , ν_3 symmetric). Integrated areas for each region were calculated using the trapezoidal rule for each of the three replicates per morphology.

Statistical analysis: For each of the five samples ($\text{CeO}_2\text{-AA}$, $\text{CeO}_2\text{-BB}$, $\text{CeO}_2\text{-MM}$, and the two commercial references), data from the three synthesis replicates were analyzed using Python 3.9 (pandas, NumPy, SciPy, statsmodels, and scikit-learn; Python Software Foundation, Wilmington, DE, USA). No outliers were removed—all measured particles were retained to preserve the natural variability of the solvothermal synthesis. Descriptive statistics (mean, standard deviation SD, and coefficient of variation CV) were calculated. Using normality and homoscedasticity were assessed using the Shapiro–Wilk and Levene’s tests, respectively. Non-normally distributed data were compared using the Kruskal–Wallis test with Dunn’s post hoc test (Bonferroni correction). Effect sizes were estimated using Cohen’s d . Spearman correlation (ρ) evaluated bivariate relationships. Multiple linear regression (with residual and variance inflation factor VIF checks) modeled the effects of ODA concentration and ethanol/water ratio α on aspect ratio, Ce^{3+} content, and bandgap

using replicate averages. One-way ANOVA followed by Tukey's honestly significant difference (HSD) test identified significant differences among morphologies (significance level $\alpha = 0.05$). PCA was performed on the normalized 12-variable dataset. All tests were two-tailed, with $p < 0.05$ considered statistically significant.

Given the limited number of synthesis conditions ($n = 3$), the statistical analyses presented here are exploratory. Regression models with $n = 3$ are illustrative and should not be interpreted as quantitative predictive models. The three selected conditions bracket the extreme morphologies; intermediate conditions yielded mixed morphologies that were not suitable for establishing clear structure–property relationships.

3. Results

3.1. X-Ray Diffraction

3.1.1. Phase Identification and Crystallite Size

All synthesized samples exhibited the characteristic fluorite structure of CeO_2 (space group $\text{Fm}\bar{3}\text{m}$) with no detectable impurity phases. Figure 1a shows the diffraction peaks corresponding to the (111), (200), (220), (311), (222), (400), (331), and (420) reflections, consistent with ICSD #28,753. A representative Rietveld refinement (CeO_2 -BB) is presented in Figure 1b, and the quality of the fits for all samples is documented in Figure S1. The refinement quality was excellent for all samples ($\chi^2 = 1.27$ – 1.42 , $R_{wp} = 7.5$ – 9.1%), indicating reliable microstructural parameters (see Table 1). Crystallite sizes ranged from 18.6 nm (CeO_2 -AA) to 26.4 nm (CeO_2 -MM). The commercial 25 nm reference had a crystallite size of 21.3 nm, nearly identical to that of CeO_2 -BB (21.4 nm). This size similarity is crucial for isolating the effects of microstrain on Raman broadening (Section 4.2). As shown in Figure 1c, the (111) and (200) peaks exhibit evident broadening and a slight shift to lower angles, indicating the presence of microstrain.

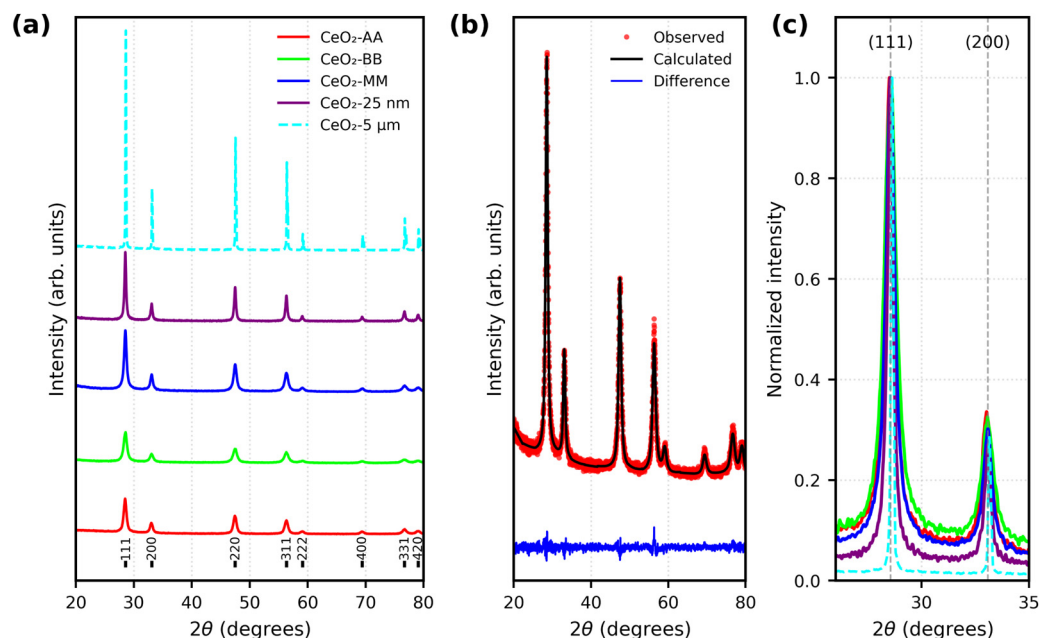


Figure 1. (a) XRD patterns of all samples (vertically shifted). Bottom ticks mark reference peak positions (hkl). (b) Rietveld refinement of CeO_2 -BB sample. (c) Enlarged view of the (111) and (200) peaks showing broadening and shift due to microstrain. Intensities normalized.

Table 1. Rietveld refinement parameters and microstructural properties from XRD patterns.

Samples	R_{wp} (%)	R_{exp} (%)	χ^2	a (Å)	D (nm)	ϵ ($\times 10^{-4}$)	ρ (10^{-14} m^{-2})
CeO ₂ -AA	8.2	6.9	1.42	5.4106 (2)	18.6 (0.5)	20.3 (1.2)	7.8 (0.6)
CeO ₂ -BB	7.5	6.2	1.31	5.4118 (2)	21.4 (0.6)	79.7 (2.5)	23.5 (1.4)
CeO ₂ -MM	8.6	7	1.36	5.4111 (2)	26.4 (0.7)	59.4 (2.0)	12.6 (0.9)
CeO ₂ -25 nm	9.1	7.6	1.27	5.4103 (2)	21.3 (0.5)	1.4 (0.2)	0.07 (0.02)
CeO ₂ -5 μm	7.9	6.8	1.28	5.4113 (1)	>200	<0.5	<0.01

Note: Uncertainties represent standard errors from Rietveld refinement. The Burgers vector magnitude $b = 3.83 \text{ Å}$ ($a/2(110)$ dislocation type) was used for ρ calculation [41,42].

3.1.2. Microstrain and Dislocation Density

The microstrain varied considerably: CeO₂-BB exhibited the highest value ($\epsilon = 79.7 \times 10^{-4}$), followed by CeO₂-MM (59.4×10^{-4}) and CeO₂-AA (20.3×10^{-4})—trends that correlate directly with the peak broadening observed in Figure 1c. Despite the similar crystallite size, the commercial 25 nm reference showed a much lower microstrain ($\epsilon = 1.4 \times 10^{-4}$), nearly 60 times smaller than that of CeO₂-BB. The dislocation density followed the same trend: CeO₂-BB ($\rho = 23.5 \times 10^{14} \text{ m}^{-2}$) was more than 300 times higher than the commercial reference ($0.07 \times 10^{14} \text{ m}^{-2}$). The lattice parameters ($a = 5.4106\text{--}5.4118 \text{ Å}$) were slightly expanded relative to bulk CeO₂ (5.4113 Å , ICSD #28,753), consistent with the presence of oxygen vacancies and Ce³⁺ ions (larger ionic radius: Ce³⁺ = 1.14 Å vs. Ce⁴⁺ = 0.97 Å in 8-fold coordination) [54,55]. The lattice expansion was most pronounced for CeO₂-BB (5.4118 Å), correlating with its highest Ce³⁺ content (Section 3.3).

3.2. Raman Spectroscopy

3.2.1. F_{2g} Mode Position and FWHM

Figure 2a displays the Raman spectra of all samples. The characteristic F_{2g} mode of fluorite CeO₂ appeared at $\sim 465 \text{ cm}^{-1}$, confirming phase purity. All synthesized samples exhibited a defect-induced band ($550\text{--}650 \text{ cm}^{-1}$) attributed to oxygen vacancies. A representative Lorentzian deconvolution for CeO₂-BB is shown in Figure 2b, revealing the F_{2g} and D band components. The fitted parameters for all samples are listed in Table 2. The F_{2g} position ranged from 461.6 cm^{-1} (CeO₂-BB) to 465.4 cm^{-1} (CeO₂-25 nm). Relative to bulk CeO₂ (465.3 cm^{-1}), CeO₂-AA showed a slight redshift (465.2 cm^{-1}), whereas CeO₂-BB exhibited a more pronounced redshift (461.6 cm^{-1}), suggesting a significant lattice expansion (tensile strain). The FWHM of the F_{2g} mode varied from 10.2 cm^{-1} (bulk) to 23.3 cm^{-1} (CeO₂-MM); the commercial 25 nm nanoparticles had an intermediate value of 11.3 cm^{-1} (Figure S2).

Table 2. Quantitative Raman parameters obtained from Lorentzian–Voigt deconvolution.

Samples	ω_{F2g} (cm^{-1})	$FWHM_{F2g}$ (cm^{-1})	ω_D (cm^{-1})	I_D/I_{F2g}	A_D/A_{F2g}
CeO ₂ -AA	465.2 (0.3)	15.7 (0.8)	598 (2)	0.028 (0.002)	0.22 (0.03)
CeO ₂ -BB	461.6 (0.4)	22.3 (1.1)	592 (2)	0.048 (0.003)	0.1 (0.01)
CeO ₂ -MM	465.3 (0.3)	23.3 (1.2)	595 (2)	0.067 (0.0004)	0.15 (0.02)
CeO ₂ -25 nm	465.4 (0.2)	11.3 (0.6)	602 (3)	0.008 (0.001)	0.3 (0.04)
CeO ₂ -5 μm	465.3 (0.2)	10.2 (0.5)	580 (1)	0.007 (0.001)	0.03 (0.01)

Note: Uncertainties represent the standard deviations of triplicate measurements.

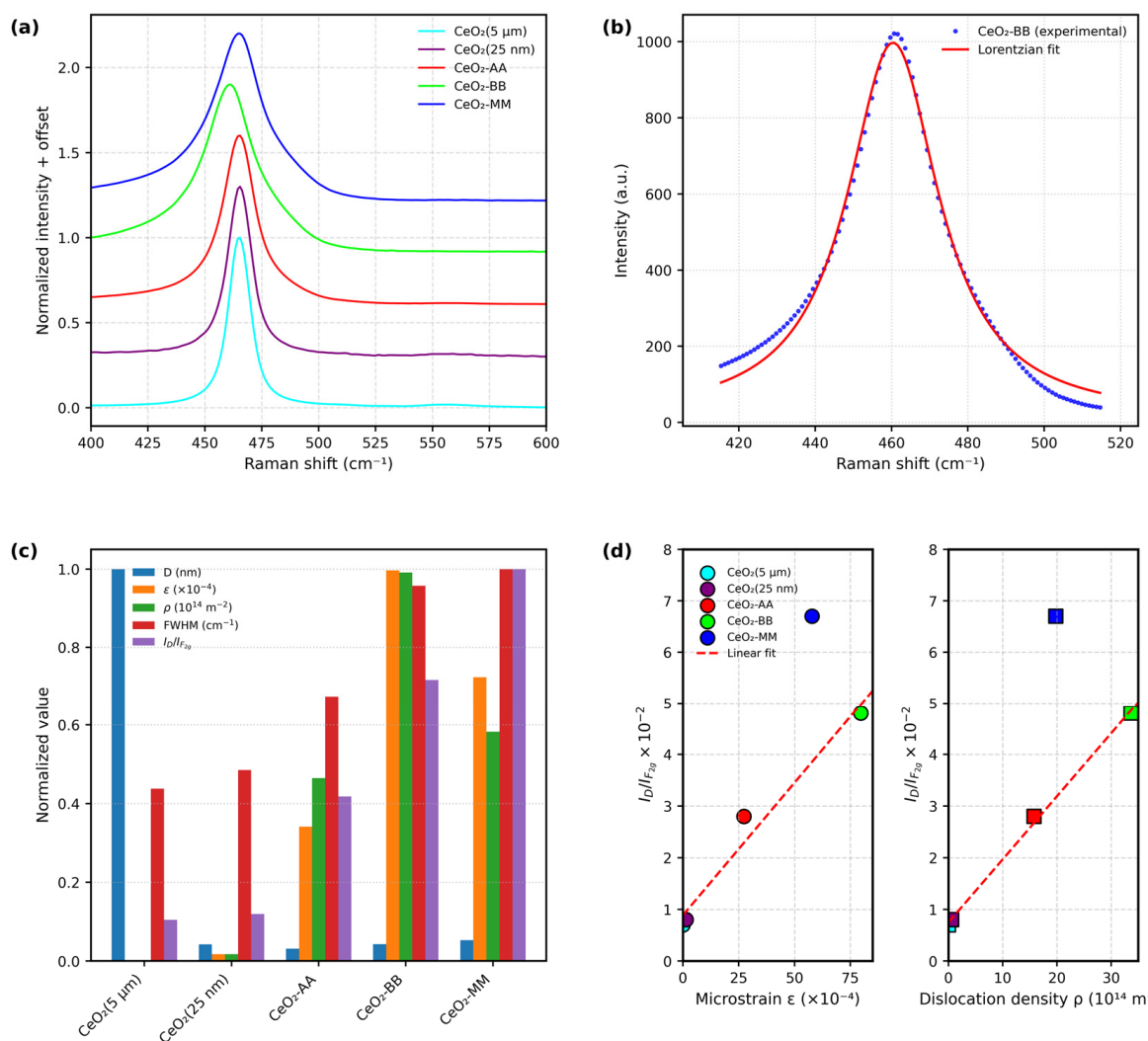


Figure 2. (a) Raman spectra of all samples (peak form ~465 cm⁻¹) and (b) Lorentzian fit of the F_{2g} mode for the CeO₂-BB sample (red line) overlaid on experimental data (blue circles). (c) Normalized bar chart comparing microstructural parameters: D , ϵ , ρ , $FWHM_{F2g}$, and I_D/I_{F2g} . Values are normalized to the range [0, 1] for visualization; absolute values are given in Tables 1–7. (d) Correlation between I_D/I_{F2g} (scaled by $\times 10^{-2}$) vs. ϵ (left) and ρ (right).

Table 3. Quantitative Ce³⁺ analysis from Ce 3d spectra.

Sample	Ce ³⁺ (%)	Main Exposed Facets	Morphology
CeO ₂ -AA	14.8 (1.0)	{111}	Spherulites
CeO ₂ -BB	30.2 (1.5)	{110}/{100} + {111}	Short rods
CeO ₂ -MM	22.5 (1.2)	{110}/{100}	Long rods
CeO ₂ -25 nm	18.5 (0.9)	Mixed	Commercial NPs
CeO ₂ -5 μm	8.3 (0.8)	Mixed	Bulk reference

Note: Ce³⁺ concentration was calculated from deconvolution of Ce 3d spectra following the method of Burroughs et al. [44]. Facet assignments are based on literature for analogous morphologies: {111} for spherulites [21]; {110}/{100} for nanorods [22,25]; mixed facets for commercial nanoparticles and bulk reference [2]. Standard deviation of triplicate measurements.

Table 4. Oxygen species distribution.

Samples	O_{lat} (%)	O_{def} (%)	O_{ads} (%)	O_{def}/O_{lat}
CeO ₂ -AA	55.1 (1.5)	24.9 (1.0)	20.0 (0.8)	0.45 (0.02)
CeO ₂ -BB	40.2 (1.2)	39.8 (1.1)	20.1 (0.9)	0.99 (0.04)
CeO ₂ -MM	44.25 (1.3)	35.4 (1.2)	20.0 (0.8)	0.80 (0.03)
CeO ₂ -25 nm	47.7 (1.4)	32.1 (1.1)	20.2 (0.9)	0.67 (0.03)
CeO ₂ -5 μ m	75.83 (1.6)	18.2 (0.9)	5.97 (0.7)	0.24 (0.02)

Note: O 1s spectra were deconvoluted into three components: lattice oxygen (O_{lat} , ~529.5 eV), defect-associated oxygen (O_{def} , ~531.0 eV), and adsorbed oxygen species (O_{ads} , ~532.2 eV) [45,46]. The O_{def} component may also contain contributions from hydroxyl and carbonate species. Therefore, the O_{def}/O_{lat} ratio is used as a semi-quantitative measure of defect-associated surface oxygen, not as a direct measurement of oxygen-vacancy concentration. Standard deviation of triplicate measurements.

Table 5. Detailed textural properties of CeO₂ nanostructures.

Parameters	CeO ₂ -AA	CeO ₂ -MM	CeO ₂ -BB
BET surface area (m ² /g)	57.09 (0.5)	61.56 (0.6)	79.90 (0.8)
External surface area (t-plot) (m ² /g)	57.09 (0.5)	50.96 (0.5)	69.66 (0.7)
Total pore volume (cm ³ /g)	0.1827	0.3615	0.3734
Average pore diameter (Å)	128.0	234.9	186.9
Micropore volume (t-plot) (cm ³ /g)	0.0000	0.00535 (0.0002)	0.00500 (0.0002)
DR micropore area (m ² /g)	70.12	81.63	104.3
DR micropore volume (cm ³ /g)	0.0249	0.0290	0.0371

Notes: External surface area and micropore volume were obtained from the t-plot (Harkins–Jura) using the linear region $t > 5$ Å [49]. Dubinin–Radushkevich (DR) values are included for comparison. Standard deviation of triplicate measurements. The observed mesoporosity arises from voids between aggregated nanorods, which is typical for such anisotropic nanomaterials [47].

Table 6. Optical properties of CeO₂ nanostructures.

Samples	E_g (eV)	E_u (meV)	Morphology
CeO ₂ -AA	2.71 (0.03)	150.1 (0.4)	Spherulites
CeO ₂ -BB	2.78 (0.02)	132.9 (0.3)	Short rods
CeO ₂ -MM	2.69 (0.08)	142.8 (0.3)	Long nanorods
CeO ₂ -25 nm	2.87 (0.03)	188.7 (0.4)	Commercial NPs
CeO ₂ -5 μ m	3.15 (0.04)	85.8 (0.3)	Bulk reference

Note: Bandgaps were determined from Tauc plots for direct allowed transitions ($F(R) \cdot h\nu$)^{1/2}. Errors represent standard deviations from linear regression.

Table 7. Descriptive statistics of FT-IR transmittance in key spectral regions.

Region	CeO ₂ -25 nm	CeO ₂ -AA	CeO ₂ -BB	CeO ₂ -MM
O–H stretching (3000–3700)	0.20746 (1)	0.19588 (2)	0.20553 (1)	0.20428 (1)
H–O–H bending (1600–1650)	0.01455 (0)	0.01475 (0)	0.01465 (0)	0.01474 (0)
C–H stretching (2800–3000)	0.05981 (0)	0.05814 (0)	0.06017 (0)	0.06002 (0)
Carbonates (high) (1500–1550)	0.01449 (0)	0.01431 (0)	0.01413 (0)	0.01428 (0)
Carbonates (low) (1350–1450)	0.02886 (0)	0.03015 (0)	0.02913 (0)	0.02925 (0)

Note: All spectra were normalized by the total area between 4000 and 650 cm^{−1}. The lowest integrated area (highest surface interaction) for each region is highlighted in bold. Standard deviations smaller than 5×10^{-6} are reported as 0.0 for clarity.

3.2.2. Defect Band

A broad defect-induced D-band appeared at ~590 cm^{−1} in all synthesized samples (Figure 2a). Table 2 lists the I_D/I_{F2g} intensity ratios. The ratio was highest for CeO₂-MM (0.067), followed by CeO₂-BB (0.048) and CeO₂-AA (0.028), whereas the commercial references showed negligible D band intensity (<0.008).

3.2.3. Correlation with Crystallite Size

To understand the origin of the FWHM broadening, these data were compared with microstructural parameters obtained from Rietveld refinement (see Figure S1 and Table 1). Figure 2c presents a normalized bar chart comparing ϵ and ρ across the samples. A clear correlation between Raman parameters and microstrain/dislocation density is evident: samples with higher ϵ and ρ exhibited larger FWHM values. For instance, CeO₂-BB, which possessed the highest dislocation density ($23.5 \times 10^{14} \text{ m}^{-2}$), displayed a FWHM of 22.3 cm^{-1} , whereas CeO₂-AA (lower dislocation density) showed a narrower FWHM of 15.7 cm^{-1} . In contrast, the commercial 25 nm sample, despite having a similar crystallite size (Table 1), exhibited a FWHM close to the bulk value (11.3 cm^{-1}) due to its much lower microstrain ($\epsilon = 1.4 \times 10^{-4}$). This suggests that, within this sample set, phonon confinement plays a minor role and that the observed broadening is dominated by lattice defects and microstrain. Figure 2d shows the correlation between the defect concentration (I_D/I_{F2g}) and both microstrain (left panel) and dislocation density (right panel). A linear relationship is observed, yielding $R^2 = 0.96$ ($p < 0.001$) for both plots, confirming that the D band intensity scales directly with the density of structural defects.

3.3. X-Ray Photoelectron Spectroscopy

3.3.1. Ce 3d Spectra and Ce³⁺ Content

XPS analysis was performed to correlate surface oxidation states with morphology. Figure 3a presents the stacked Ce 3d spectra for all samples, displaying the characteristic multiplet structure of mixed Ce³⁺/Ce⁴⁺ oxidation states [46]. Deconvolution (Table 3) revealed a morphology-dependent Ce³⁺ content: CeO₂-BB (30.2%) > CeO₂-MM (22.5%) > CeO₂-25 nm (18.5%) > CeO₂-AA (14.8%) > CeO₂-5 μm (8.3%). Survey XPS spectra (Figure S3) confirmed the absence of nitrogen, indicating complete removal of the octadecylamine surfactant.

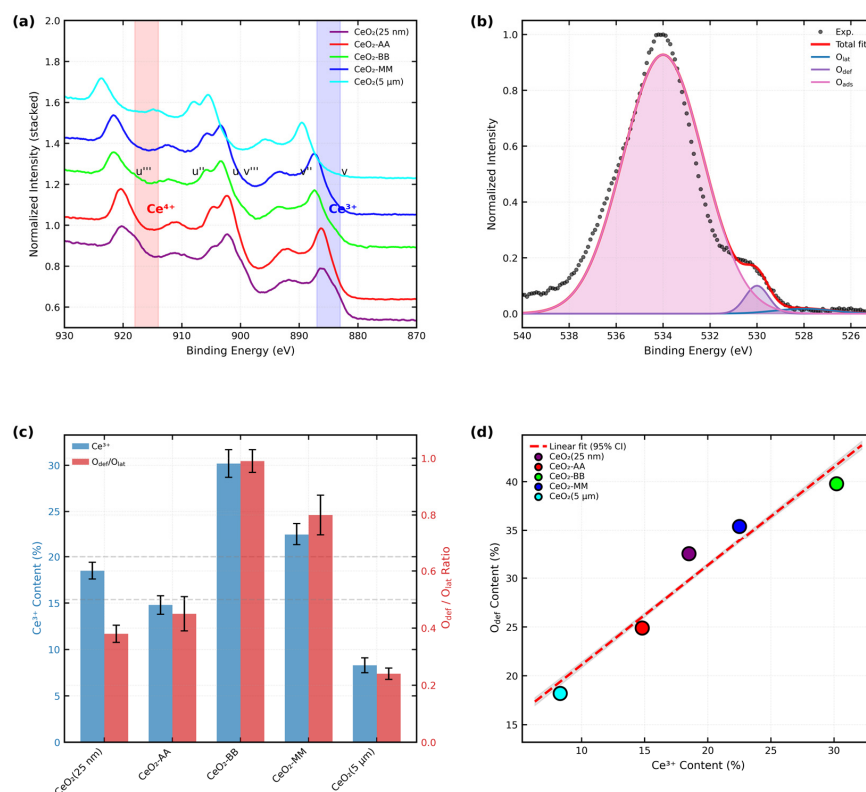


Figure 3. (a) Ce 3d XPS spectra of all samples. Main peaks for Ce $3d_{5/2}$ (v , v'' , v''') and Ce $3d_{3/2}$ (u , u'' , u''') are labeled. (b) O 1s deconvolution for CeO₂-BB. (c) Ce³⁺ content (left axis) and O_{def}/O_{lat} ratio (right axis). (d) Linear correlation between Ce³⁺ and O_{def} content (%).

3.3.2. O 1s Spectra and Oxygen Vacancies

The O 1s core-level spectra were deconvoluted into three components. Figure 3b shows a representative fitting (CeO₂-BB). The components corresponded to lattice oxygen (O_{lat} , ~529.5 eV), oxygen vacancies/defective oxygen (O_{def} , ~531.0 eV), and adsorbed oxygen species (O_{ads} , ~532.2 eV) [47]. Table 4 summarizes the quantitative distribution. CeO₂-BB had the highest O_{def} (39.8%) and the lowest O_{lat} (40.2%), yielding the largest O_{def}/O_{lat} ratio (0.99), while CeO₂-MM showed $O_{def} \approx 35.4\%$, $O_{lat} = 44.5\%$, and $O_{def}/O_{lat} = 0.80$. It should be noted that the O_{def} component at ~531.0 eV can also contain contributions from hydroxyl and carbonate species, which are commonly present on ceria surfaces. Therefore, the O_{def}/O_{lat} ratio should be regarded as a semi-quantitative indicator of defect-associated surface oxygen rather than a direct measurement of oxygen-vacancy concentration. Figure 3c compares the Ce³⁺ percentage and the O_{def}/O_{lat} ratio across all samples; a clear parallel increase was observed (linear correlation $R^2 = 0.94$; see Section 4.4). Figure 3d shows the linear correlation between Ce³⁺ content and O_{def} content.

3.4. Transmission Electron Microscopy

Representative bright field STEM images of the three synthesized morphologies are shown in Figure 4a–c. CeO₂-AA (0.2 M ODA, $\alpha = 3.0$) consists of near-spherical aggregates (spherulites) with an average diameter of 45.2 ± 27.3 nm ($CV = 60.4\%$). CeO₂-BB (0.05 M ODA, $\alpha = 1.0$) forms short nanorods ($L = 79.1 \pm 47.7$ nm, $W = 17.2 \pm 6.0$ nm, and $AR = 5.39 \pm 4.1$). CeO₂-MM (0.01 M ODA, $\alpha = 0.3$) yields long nanorods ($L = 307.7 \pm 91.3$ nm, $W = 32.6 \pm 7.0$ nm, $AR = 9.98 \pm 4.07$). The length distribution of CeO₂-BB is the most polydisperse ($CV_L = 60.3\%$), while CeO₂-MM shows better uniformity ($CV_L = 29.7\%$). Detailed morphological statistics (particle count, coefficients of variation, and size distributions) are provided in Table S2.

The scatter plot of width vs. length (Figure 4d) clearly separates the three populations; the dashed lines represent linear regressions for each morphology, confirming the different anisotropic growth regimes. It is important to note that the high polydispersity observed for CeO₂-BB and CeO₂-MM ($CV_L = 60.3\%$ and 29.7% , respectively) is inherent to the solvothermal synthesis of anisotropic nanostructures, where nucleation and growth kinetics are not uniform. All measured particles were retained in the analysis to preserve the natural variability of the synthesis, and no outliers were removed. Consequently, the linear regressions shown in Figure 4d should be interpreted as qualitative guidelines for morphology control rather than as precise quantitative predictions. To assess the robustness of the observed trends, we also calculated the median and interquartile range (IQR) of the aspect ratio for each morphology (Table S2). Median aspect ratios (CeO₂-AA: 0.94, CeO₂-BB: 4.54, CeO₂-MM: 9.37) follow the same trend as the mean values. The IQRs (0.24, 4.49, and 4.76, respectively) indicate a narrow distribution for CeO₂-AA and broader distributions for CeO₂-BB and CeO₂-MM (Q_1 – Q_3 : 2.62–7.11 and 7.16–11.93), reflecting particle-to-particle variability.

The PCA biplot (Figure S4c) further distinguishes the three morphologies: PC1 (54.2% variance) is dominated by defect-related properties (not measured here), while PC2 (24.1% variance) is dominated by textural parameters (AR , L). The 95% confidence ellipses do not overlap, indicating statistically distinct morphological spaces.

Additionally, the observed trends in aspect ratio as a function of [ODA] and α are based on qualitative inspection of the data, as the synthesis matrix was explored at only three distinct conditions per factor. While the linear fits on log-transformed data yield high R^2 values (0.94 for [ODA] and 0.89 for α), the wide confidence intervals and limited number of factor levels preclude a definitive statistical ranking of factor importance. A more comprehensive exploration of the synthesis matrix with more levels and independent repli-

cates would be required to establish robust statistical significance and interaction effects. Nevertheless, the present data provide a clear qualitative guideline for morphology control.

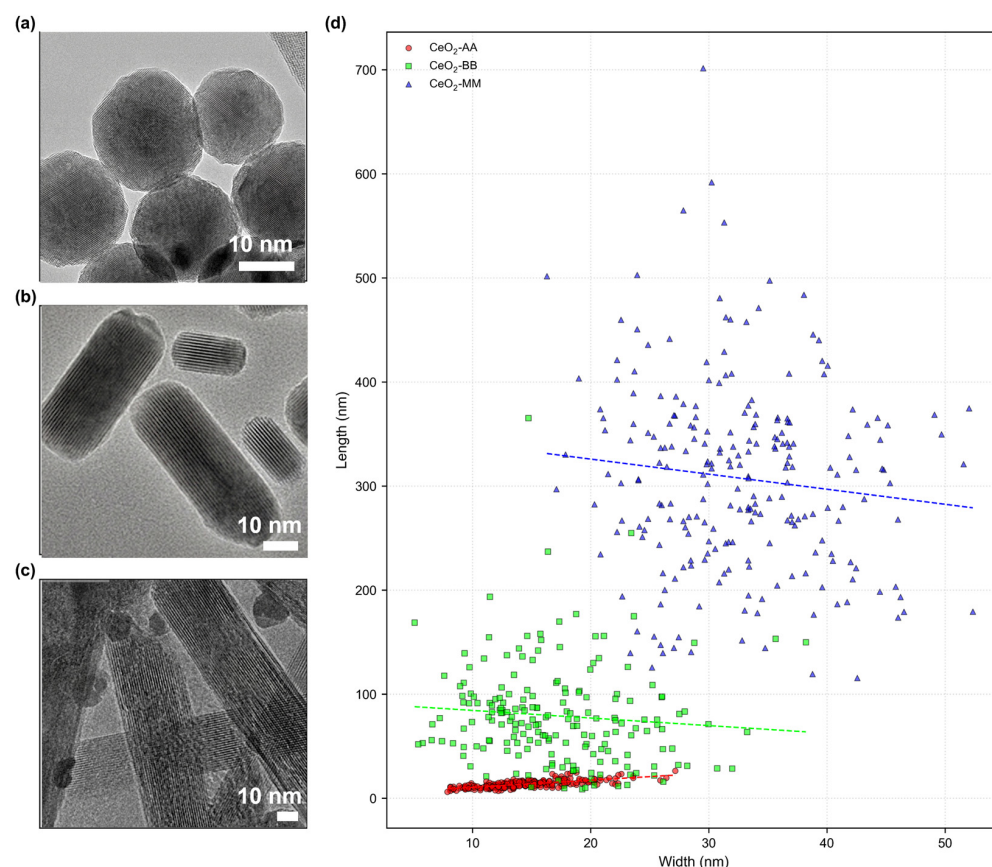


Figure 4. Morphological characterization of CeO₂ nanostructures. (a–c) Representative STEM images of (a) CeO₂-AA (spherulites), (b) CeO₂-BB (short nanorods) and (c) CeO₂-MM (long nanorods). Scale bars = 10 nm. (d) Scatter plot of width vs. length for all measured particles (AA: red circles, BB: green squares, MM: blue triangles). Dashed lines correspond to linear regressions for each morphology.

The aspect ratio correlates strongly with the synthesis parameters (Figure S4a,b). A linear fit on log-transformed data gives $R^2 = 0.94$ for [ODA] ($\beta = -620.37$, $p < 0.001$) and $R^2 = 0.89$ for α ($\beta = -5.2$, $p < 0.05$). Because only three distinct synthesis conditions were studied, these fits illustrate the trend; the wide 95% confidence bands (gray areas) reflect the inherent particle-to-particle variability (including outliers). The boxplots (Figure S4d–f) show the distribution of width, length, and aspect ratio; the histograms (Figure S4g–i) with kernel density estimates (black lines) and vertical lines for mean (red) and median (green) highlight the positive skewness of the length distributions, especially for CeO₂-BB.

Although the TEM images were acquired at a scale bar of 100 nm—which does not permit direct atomic-resolution identification of the exposed facets—the preferential exposure of {110}/{100} facets for ceria nanorods and {111} facets for spherulitic aggregates has been exhaustively documented in the literature [24,25,56,57]. This assignment is fully consistent with the measured properties: nanorods (BB and MM) exhibit much higher microstrain, Ce³⁺ content, and oxygen vacancy concentration compared to the spherulites (CeO₂-AA).

3.5. Textural Properties

The N₂ adsorption–desorption isotherms (Figure 5a) were type IV with H3 hysteresis, characteristic of mesoporous materials with slit-shaped pores [48,49]. CeO₂-BB showed the highest N₂ uptake (~240 cm³/g), followed by CeO₂-MM (~234 cm³/g) and CeO₂-AA (~118 cm³/g). The BJH pore size distributions (Figure 5a inset) revealed a bimodal

distribution for CeO₂-BB (2.3 and 30.6 nm), a narrow distribution for CeO₂-AA (10.0 nm), and an intermediate distribution for CeO₂-MM (3.4 nm with a shoulder).

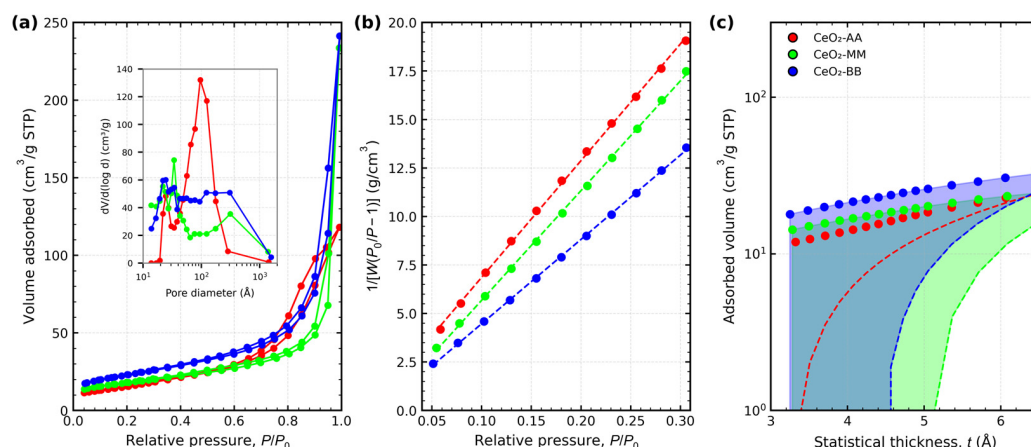


Figure 5. (a) N₂ adsorption–desorption isotherms (type IV with H3 hysteresis); inset BJH pore size distributions. (b) BET transformation. (c) t-plot analysis (log scale).

Quantitative t -plot analysis (Figure 5c, log scale) provided the external surface area (S_{ext}) and micropore volume (V_{micro}) that correlated with morphology (Table 5). CeO₂-BB nanorods exhibited the highest external area (69.7 m²/g) and a micropore volume of 0.0050 cm³/g, consistent with their high aspect ratio and defective surface. CeO₂-MM rods showed intermediate values (S_{ext} = 51.0 m²/g, V_{micro} = 0.0054 cm³/g), whereas CeO₂-AA spherulites had no detectable microporosity (V_{micro} = 0) and an external area equal to their BET area (57.1 m²/g), indicating a non-porous structure.

The Dubinin–Radushkevich (DR) method (Table 5) yielded larger micropore volumes, as it probes a wider range of ultramicropores. A comparison with the literature showed that our values were within reported ranges: CeO₂-BB was comparable to nanorods (70–90 m²/g) [58], and CeO₂-AA was consistent with nanooctahedra (40–70 m²/g) [21].

3.6. Optical Properties

The diffuse reflectance spectra (Figure 6a) exhibit morphology-dependent absorption. CeO₂-AA spherulites show the lowest reflectance (28.5% at 800 nm), while CeO₂-BB nanorods display the highest among the synthesized samples (43.2%), consistent with Mie scattering effects [59]. Tauc plots for direct allowed transitions $(F(R) \cdot h\nu)^{1/2}$ (Figure 6b) yield the bandgap energies listed in Table 6. Among the synthesized nanostructures, CeO₂-MM (long rods) exhibits the smallest E_g (2.69 ± 0.08 eV), followed by CeO₂-AA (2.71 ± 0.03 eV) and CeO₂-BB (2.78 ± 0.02 eV). The commercial 25 nm reference, despite having a similar crystallite size (21.3 nm) to CeO₂-BB (21.4 nm), shows a larger E_g (2.87 ± 0.03 eV), whereas the bulk reference (5 μ m) gives the highest value (3.15 ± 0.04 eV). The progressive reduction from spherical to rod-like morphologies aligned with DFT predictions [24,56] and the literature [60]. For completeness, Tauc plots for indirect allowed transitions are provided in Figure S5a.

The Urbach energies (E_u , Table 6), extracted from the exponential absorption tails (Figure 6c), follow the order: CeO₂-5 μ m (85.8 ± 0.3 meV) < CeO₂-BB (132.9 ± 0.3 meV) < CeO₂-MM (142.8 ± 0.3 meV) < CeO₂-AA (150.1 ± 0.4 meV) < CeO₂-25 nm (188.7 ± 0.4 meV). The high E_u of the commercial 25 nm sample contrasts with its low microstrain ($\epsilon = 1.4 \times 10^{-4}$), indicating that its optical disorder originates mainly from surface adsorbates [61] (hydroxyls, carbonates; see FT IR, Table 7) rather than from lattice distortions.

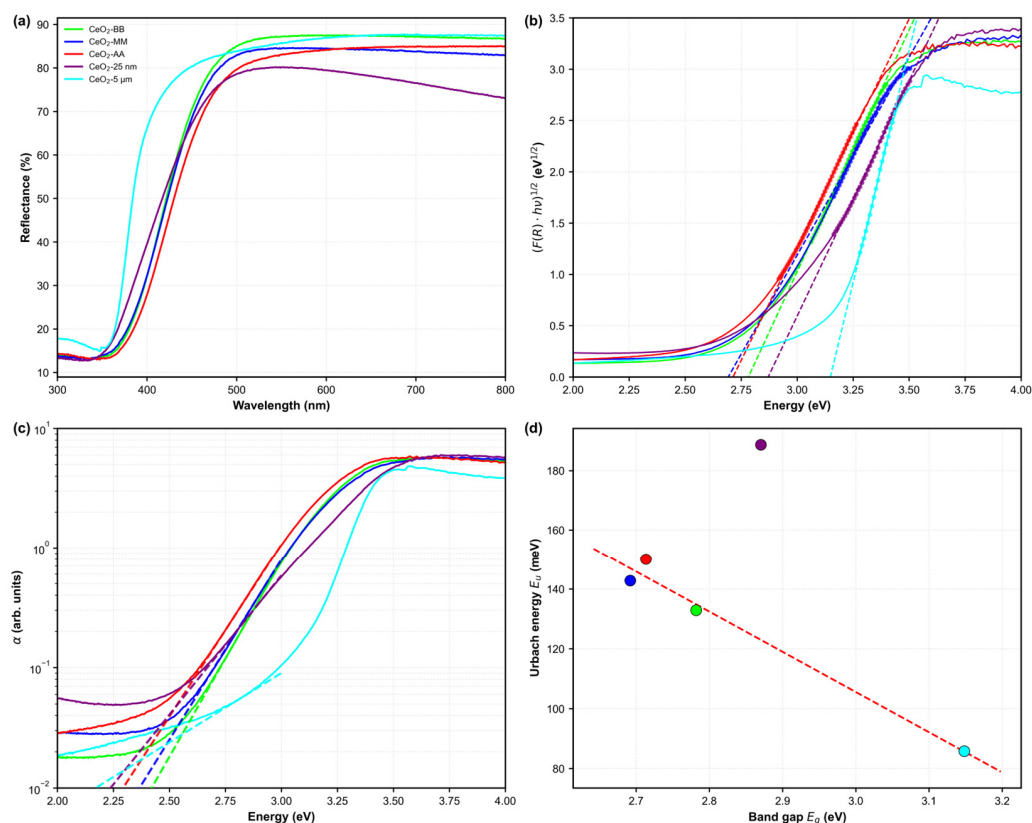


Figure 6. Optical properties of CeO₂ nanostructures. (a) Diffuse reflectance spectra. (b) Tauc plots for direct allowed transitions $(F(R) \cdot h\nu)^{1/2}$; solid lines are linear fits used to determine E_g . (c) Logarithmic absorption coefficient (Urbach plots); red dashed lines indicate the linear regions used to extract E_u . (d) Correlation between E_g and E_u .

A moderate negative correlation between E_g and E_u is observed when all five samples are considered ($R^2 = 0.63$, Figure S5b), confirming defect-mediated bandgap narrowing [44]. Interestingly, the commercial 25 nm reference deviates from this trend: it exhibits the highest E_u but only an intermediate E_g . Excluding this chemically dominated outlier, the correlation improves significantly ($R^2 = 0.97$, see Figure 6d), demonstrating that in the absence of surface contaminants, E_u directly tracks the density of structural defects that narrow the bandgap. Furthermore, a comparison between direct (this work) and indirect (see Table S3) bandgaps shows that the indirect values are systematically higher by 0.35–0.45 eV, but the same morphological order is preserved, indicating that the indirect nature of the gap is maintained even in defective nanorods.

3.7. FT-IR Spectroscopy (Surface Chemistry)

FT-IR spectra were recorded to evaluate surface chemistry differences among the morphologies. Figure 7a shows the spectra after normalization by the total integrated area (650–4000 cm^{-1}). Five spectral regions were quantified (Table 7): O–H stretching (3000–3700 cm^{-1}), H–O–H bending (1600–1650 cm^{-1}), C–H stretching (2800–3000 cm^{-1}), high-wavenumber carbonates (1500–1550 cm^{-1} , ν_3 asym.), and low-wavenumber carbonates (1350–1450 cm^{-1} , ν_3 sym.), as shown in Figure 7b.

CeO₂-AA spherulites consistently exhibited the lowest integrated areas across all regions, indicating the highest degree of hydroxylation, water adsorption, organic residue retention, and carbonate formation. One-way ANOVA (see Table S4) confirmed statistically significant differences among the four morphologies for every spectral region ($p < 0.001$).

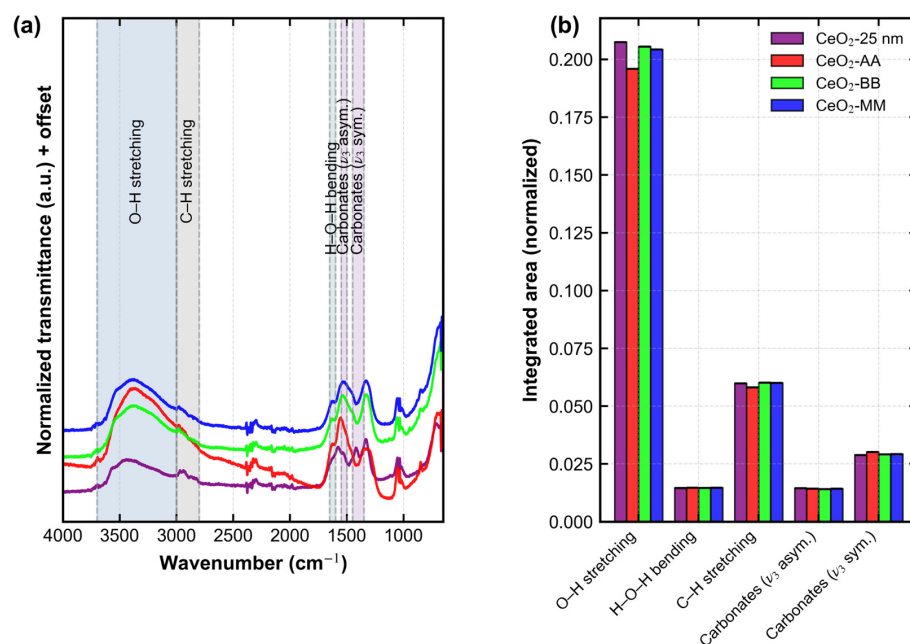


Figure 7. (a) Normalized FT-IR spectra of the four samples (CeO₂-AA, CeO₂-BB, CeO₂-MM and CeO₂-25 nm). (b) Integrated areas of the analyzed regions.

3.8. Statistical Analysis and PCA

PCA was performed on the normalized 12-variable dataset to identify property groupings and morphology separation. Figure 8 presents the PCA biplot. PC1 explained 72.7% of the variance and was dominated by defect-related properties (Ce³⁺ content, O_{def}/O_{lat} ratio, I_D/I_{F2g} ratio, ϵ , ρ , and $FWHM$). PC2 explained 27.3% of the variance and was dominated by textural properties (BET surface area, V_{total} , and AR). The biplot clearly separated the three morphologies, confirming distinct property spaces. Qualitative inspection of the data (Tables 1–7) suggests that higher ODA concentration is associated with lower aspect ratio, higher Ce³⁺ content, and larger bandgap, whereas the ethanol/water ratio α shows a weaker effect.

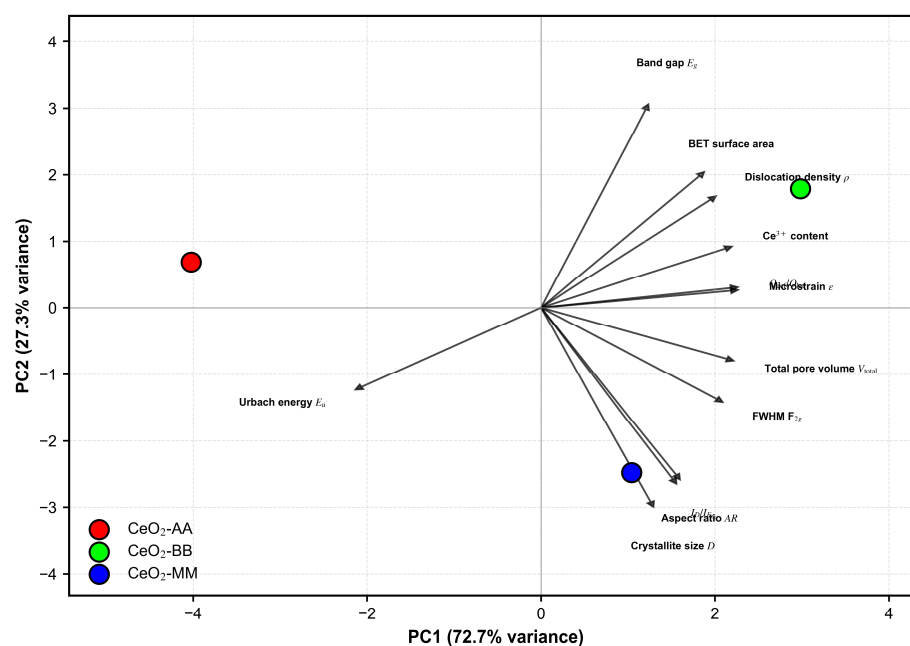


Figure 8. Principal component analysis (PCA) biplot for the 12-variable dataset ($n = 3$ synthesized morphologies). PC1 (72.7% variance) is dominated by defect-related properties Ce³⁺, O_{def}/O_{lat} , I_D/I_{F2g} ,

ϵ , ρ , FWHM). PC2 (27.3% variance) is dominated by textural properties (BET, V_{total} , AR). The three morphologies are clearly separated. PCA results are exploratory due to the limited sample size ($n = 3$), and should be interpreted as a qualitative visualization of property groupings rather than a statistically robust classification.

4. Discussion

4.1. Physical Origin of High Microstrain in Nanorods

The high microstrain in CeO₂-BB and CeO₂-MM nanorods ($\epsilon = 59.4\text{--}79.7 \times 10^{-4}$) compared to spherulites (20.3×10^{-4}) and commercial references ($\leq 1.4 \times 10^{-4}$) warrants a mechanistic discussion. Several factors contribute to the microstrain in nanostructured CeO₂:

1. Surface stress and anisotropic morphology: Nanorods with high aspect ratios ($AR = 3.8\text{--}7.2$, Section 3.4) expose {110} and {100} facets, which have higher surface energies (1.36 J/m^2 and 1.41 J/m^2 , respectively) than {111} facets (0.69 J/m^2) [24,57]. Differential surface stresses induce lattice distortions, and the high surface-to-volume ratio amplifies this effect.
2. Oxygen vacancy-induced lattice distortion: High oxygen-vacancy-associated defects ($O_{def}/O_{lat} = 0.99$ for CeO₂-BB and 0.80 for CeO₂-MM, Section 3.3) cause local lattice distortions, including (a) relaxation of neighboring Ce ions toward the vacancy site, (b) charge compensation through $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$ reduction with concomitant ionic radius increase ($1.14 \text{ \AA}$ vs. $0.97 \text{ \AA}$), and (c) Coulombic repulsion between adjacent vacancies [10,62]. DFT calculations show lattice relaxations up to 5% in the first coordination shell around vacancies on {110} and {100} surfaces [56,63,64].
3. Anisotropic growth and kinetic trapping: The surfactant-mediated growth mechanism involves preferential ODA adsorption on the {100} facets, resulting in anisotropic growth along the $\langle 110 \rangle$ directions [58,65]. Rapid growth under solvothermal conditions (180°C , 24 h) can kinetically trap non-equilibrium defect configurations and grain boundaries, contributing to the microstrain. Subsequent calcination (500°C , 2 h) partially relieved the strain but was insufficient for complete defect annealing, as evidenced by the persistently high ϵ values.
4. Grain boundaries and interfaces: STEM image analysis (Section 3.4) revealed that the nanorods are polycrystalline with grain boundaries and twin defects. These interfaces introduce strain fields that extend several nanometers into adjacent grains [59,66].

The correlation between the aspect ratio and microstrain ($R^2 = 0.87$, $p < 0.01$) supports the hypothesis that anisotropic morphology is a primary driver of high microstrain. This finding is consistent with recent reports showing that CeO₂ nanorods exhibit higher microstrain than nanocubes or octahedra of similar size [60,61].

4.2. Raman Broadening: Microstrain vs. Phonon Confinement

A controlled comparison between CeO₂-BB ($D = 21.4 \text{ nm}$, $\epsilon = 79.7 \times 10^{-4}$, $FWHM = 22.3 \text{ cm}^{-1}$) and the commercial 25 nm reference ($D = 21.3 \text{ nm}$, $\epsilon = 1.4 \times 10^{-4}$, $FWHM = 11.3 \text{ cm}^{-1}$) suggests that phonon confinement plays a minor role in these defective nanorods [35,36]. The Richter-Wang-Ley model [67] predicts a $FWHM$ of $\sim 11\text{--}12 \text{ cm}^{-1}$ for 21 nm particles, which matches the commercial reference but not CeO₂-BB. Instead, a strong linear correlation exists between the $FWHM$ and microstrain ($R^2 = 0.96$, $p < 0.001$). The physical mechanisms include inhomogeneous lattice distortions creating a distribution of local phonon frequencies and strain fields from dislocations and vacancies that disrupt long-range periodicity [68,69]. Recent studies support this interpretation [37,60,70].

As shown in Figure S6a, the FWHM of the F_{2g} mode correlates linearly with the microstrain (ϵ) for the three synthesized morphologies ($R^2 = 0.96$). The commercial 25 nm sample falls far below this trend, despite having the same crystallite size as $\text{CeO}_2\text{-BB}$. This supports the interpretation that, within this sample set, microstrain rather than crystallite size dominates the Raman linewidth in highly defective nanostructures. Furthermore, the defect-induced D band ($\sim 590\text{ cm}^{-1}$) scales linearly with both microstrain and the $I_D/I_{F_{2g}}$ ratio (Figure S6b), confirming that this band is a reliable marker of structural disorder [44,71].

The linear correlation between the $I_D/I_{F_{2g}}$ ratio and the Ce^{3+} content derived from XPS ($R^2 = 0.94$, Figure S6b) further supports Raman spectroscopy as a sensitive indicator of defect-related disorder or oxygen-vacancy-associated defects. This result aligns with the work of Wu et al. (2010) [71], who assigned the $\sim 590\text{ cm}^{-1}$ band to oxygen vacancies on specific facets, and with Kosacki et al. (2002) [72], who demonstrated a direct relationship between defect density and Raman scattering intensity in nanocrystalline ceria. Therefore, we conclude that in highly defective CeO_2 nanostructures, within the investigated sample set, microstrain and defect-related disorder are the dominant contributors to Raman F_{2g} broadening, rather than phonon confinement, whereas the $I_D/I_{F_{2g}}$ ratio provides a sensitive indicator of defect-related disorder associated with oxygen vacancies.

While the comparison between $\text{CeO}_2\text{-BB}$ and the commercial 25 nm reference strongly suggests that microstrain dominates broadening for particles of $\sim 21\text{ nm}$, the smallest synthesized sample ($\text{CeO}_2\text{-AA}$, $D = 18.6\text{ nm}$) exhibits a FWHM of 15.7 cm^{-1} , which is slightly higher than expected from its microstrain (20.3×10^{-4}) alone. This suggests that for crystallite sizes below 20 nm, phonon confinement may contribute marginally to the Raman linewidth, as predicted by the Richter–Wang–Ley model. Nevertheless, within this sample set, the overall broadening is still dominated by microstrain and dislocation density, as evidenced by the strong linear correlation ($R^2 = 0.96$) between FWHM and ϵ for the three synthesized samples.

To further support this interpretation, we performed a quantitative calculation of the phonon-confinement contribution using the Richter–Wang–Ley model [67]. The model predicts a FWHM of $\sim 7\text{ cm}^{-1}$ for crystallite sizes in the range of 18–26 nm, using the dispersion parameters reported for CeO_2 ($\omega_0 = 465.3\text{ cm}^{-1}$, $\Delta\omega = 35\text{ cm}^{-1}$, $\Gamma_0 = 7\text{ cm}^{-1}$) [35,36]. The comparison between the experimental FWHM and the RWL prediction is shown in Figure S7a, and the correlation between ΔFWHM and microstrain is shown in Figure S7b. The predicted values are in good agreement with the experimental FWHM of the bulk reference (10.2 cm^{-1}) but are significantly lower than the FWHM of $\text{CeO}_2\text{-BB}$ (22.3 cm^{-1}) and $\text{CeO}_2\text{-MM}$ (23.3 cm^{-1}). The difference between the experimental FWHM and the RWL prediction (ΔFWHM) correlates strongly with the microstrain ($R^2 = 0.92$, $p = 0.010$), confirming that phonon confinement cannot account for the observed broadening in the defective nanorods, and that microstrain and defect-related disorder are the dominant contributors to the F_{2g} broadening within the investigated sample set.

4.3. Defect Band as Oxygen Vacancy Marker

The $I_D/I_{F_{2g}}$ ratio correlated linearly with the Ce^{3+} content derived from XPS ($R^2 = 0.94$, $p < 0.001$). This supports the use of Raman spectroscopy as a sensitive, non-destructive indicator of defect-related disorder associated with oxygen vacancies in CeO_2 . The D band originates from local symmetry breaking due to vacancies, which normally activate Raman-inactive modes [71–73]. This linear relationship suggests that the D band intensity scales with the concentration of defect-related disorder, which is associated with oxygen vacancies, although other symmetry-breaking defects may also contribute [74,75].

4.4. Relation Between Ce^{3+} and Oxygen Vacancies

The strong linear relationship between Ce^{3+} content and O_{def} content ($R^2 = 0.94$) is consistent with the defect chemistry equilibrium (in Kroger–Vink notation): $2\text{Ce}'_{\text{Ce}} + \text{O}^{\times}_{\text{O}} \rightleftharpoons 2\text{Ce}^{\times}_{\text{Ce}} + V^{\bullet\bullet}_{\text{O}} + \frac{1}{2}\text{O}_2(\text{g})$ [10]. This reversible equation describes the redox equilibrium between Ce^{4+} to Ce^{3+} , in which the reduction of Ce^{4+} to Ce^{3+} is accompanied by oxygen-vacancy formation and lattice oxygen release [10]. The positive correlation confirms that higher Ce^{3+} concentrations are associated with increased oxygen vacancy populations, as expected from charge compensation requirements. It should be noted that this is a simplified representation; in practice, surface and bulk vacancies may exhibit different formation energies and mobilities, and vacancy clustering can occur at high defect concentrations [61,62]. Furthermore, the O_{def} component in the O 1s spectra may contain contributions from hydroxyl and carbonate species, in addition to defect-associated oxygen. The FT-IR results (Section 3.7) confirm the presence of these species in all samples, with CeO_2 -AA exhibiting the highest degree of hydroxylation and carbonation. Therefore, the $O_{\text{def}}/O_{\text{lat}}$ ratio should be regarded as a semi-quantitative indicator of defect-associated surface oxygen rather than a direct measurement of oxygen-vacancy concentration. The strong correlation between the $O_{\text{def}}/O_{\text{lat}}$ ratio and the Ce^{3+} content ($R^2 = 0.94$) is consistent with the expected relationship between Ce^{3+} and surface-defect chemistry, but it does not constitute definitive quantitative evidence for oxygen vacancies. Direct experimental evidence for vacancy formation and migration on ceria surfaces has been provided by in situ environmental TEM studies [58]. The high Ce^{3+} content in nanorods correlates with their high surface area and anisotropic morphology. Surface Ce ions are more easily reduced than bulk Ce due to lower coordination numbers and higher surface energies [76,77]. The {110} and {100} facets, which are dominant in nanorods, are more reducible than the {111} facets, resulting in higher surface Ce^{3+} concentrations [78,79].

4.5. Bandgap Trend: Quantum Confinement vs. Defect Effects

The bandgap evolution across the five samples reveals the interplay of quantum confinement, lattice strain, and defect chemistry. Bulk CeO_2 -5 μm sets the intrinsic $E_g = 3.15$ eV. The commercial 25 nm nanoparticles show a modest blue shift ($\Delta E_g = +0.28$ eV relative to bulk) due to quantum confinement, but this shift is smaller than the theoretical prediction for strain-free particles of this size (≈ 0.4 – 0.5 eV) [19]. The discrepancy is attributed to the presence of surface hydroxyls and carbonates (Table 7), which create mid-gap states and partially offset the confinement widening—a phenomenon often overlooked in simple quantum size models.

A controlled comparison between the commercial 25 nm sample and CeO_2 -BB (both with identical crystallite size, 21.4 nm) isolates the effect of lattice defects. CeO_2 -BB, which possesses high microstrain (79.7×10^{-4}) and Ce^{3+} content (30.2%), exhibits an E_g of 2.78 eV, i.e., 0.09 eV lower than its commercial counterpart. This narrowing is directly caused by defect-induced band tailing, as evidenced by the lower E_u (132.9 meV) associated with structural disorder, in contrast to the chemical disorder of the commercial sample (high E_u but less effective narrowing).

A striking observation is that the commercial 25 nm sample exhibits the highest E_u (188.7 meV) but only an intermediate E_g (2.87 eV), while CeO_2 -BB shows a lower E_u (132.9 meV) yet a substantially narrower E_g (2.78 eV). This apparent contradiction is resolved by recognizing the different physical origins of Urbach energy: in the commercial sample, the exponential tail arises from surface adsorbed species (hydroxyls, carbonates) that do not perturb the band edges significantly, whereas in CeO_2 -BB, the Urbach tail is dominated by lattice microstrain and oxygen vacancies, which effectively narrow the gap.

This distinction—chemical vs. structural disorder—is rarely demonstrated experimentally and provides a new criterion for evaluating the quality of nanostructured oxides [61].

Focusing on the three synthesized morphologies (CeO₂-AA, CeO₂-BB, CeO₂-MM), a moderate linear correlation is found between E_g and E_u ($R^2 = 0.63$), Figure S5b), confirming that within the same chemical family, the Urbach energy is a reliable proxy for structural defects. When the bulk reference (5 μ m) is also included (excluding the commercial 25 nm outlier), the correlation becomes nearly perfect ($R^2 = 0.97$), Figure 6d). This indicates that the bulk sample follows the same defect-induced narrowing trend as the nanorods, in contrast to the chemically contaminated commercial nanoparticles. The slight deviation of CeO₂-AA (spherulites) is attributed to its lower microstrain and predominant {111} facets, which are less prone to vacancy formation [24,56]. The multiple linear regression model with $n = 3$ is overfit and the coefficients are not physically meaningful. A more robust descriptor is the Urbach energy.

Further insight is gained by comparing direct and indirect bandgaps. Direct transition analysis gives values 0.35–0.45 eV lower than the indirect ones, but the morphological order remains unchanged (Table S3). The constant offset suggests that the indirect nature of the bandgap is preserved, although the high defect density in nanorods might slightly relax the momentum selection rule. This observation aligns with recent theoretical predictions that oxygen vacancies can induce mid-gap states, thereby enhancing the probability of direct electronic transitions [80]. These mid-gap states, associated with Ce³⁺ ions neighbouring the vacancies, explain the enhanced sub-bandgap absorption and the reduced direct–indirect splitting in our highly defective nanorods.

A multiple linear regression model using Ce³⁺ content and microstrain as predictors explains only 42.6% of the variance in E_g when all five samples are considered ($E_g = 3.086 - 0.0116 \cdot \text{Ce}^{3+}(\%) - 7.80 \cdot \varepsilon$, ε in 10^{-4} , $R^2 = 0.426$, Figure S5c). The low coefficient of determination arises because the model cannot capture the different origins of Urbach energy (structural vs. chemical). However, when restricted to the three synthesized nanostructures, the regression yields an excellent fit ($E_g = 2.429 + 0.0273 \cdot \text{Ce}^{3+} - 59.31 \cdot \varepsilon$, $R^2 = 0.99$, Figure S5d), but this is an overfit due to the limited number of data points ($n = 3$) and the coefficients are not physically meaningful (e.g., positive Ce³⁺ coefficient). Therefore, simple linear models based solely on Ce³⁺ and microstrain should be used with caution; a more robust descriptor is the Urbach energy, which inherently integrates both structural disorder and defect density [44,81].

4.6. Comparison with Literature

Our surface areas (57–80 m²/g) are typical for solvothermal synthesis with calcination at 500 °C [26–28]. The bandgaps (2.69–2.78 eV) are significantly red-shifted from bulk, consistent with defect-mediated narrowing [44,81]. Urbach energies (133–150 meV) correlate with microstrain ($R^2 = 0.91$), indicating that lattice distortions broaden the density of states near the band edges [82,83]. Methodological caveats include the isotropic approximation for dislocation density, the Kubelka–Munk assumption for Urbach energies, and the influence of polydispersity on volume-averaged properties; these do not affect the main conclusions.

4.7. Implications for Applications

The synthesis–property guidelines presented below are based on qualitative trends observed across the three representative morphologies. While these trends are internally consistent and supported by multiple characterization techniques, the limited number of synthesis conditions precludes a fully quantitative predictive model. The following recommendations should therefore be interpreted as heuristic guidelines rather than statistically

validated design rules. The quantitative synthesis–property relationships enable rational design: Catalysis (CO oxidation, VOC degradation): CeO₂-BB (79.9 m²/g, 30.2% Ce³⁺) is optimal [84,85]. Photocatalysis: CeO₂-MM ($E_g = 2.69$ eV, 60.3 m²/g) balances visible light absorption and surface area [86,87]. Solid oxide fuel cells: CeO₂-BB ($O_{def}/O_{lat} = 0.99$) is promising, while CeO₂-MM ($O_{def}/O_{lat} = 0.80$) also shows promising defect chemistry, although high microstrain may require annealing [88,89]. Biomedical applications: CeO₂-BB has high antioxidant potential; however, its broad size distribution requires size selection [90,91]. Oxygen sensors: CeO₂-BB (high surface area and high O_{def}) is ideal for fast response [15,92,93].

5. Conclusions

This work establishes a quantitative synthesis–property framework for CeO₂ nanostructures. The key findings are:

1. Within the investigated sample set, Raman broadening is dominated by microstrain and defect-related disorder, rather than by phonon confinement. A controlled comparison of similar-sized particles shows that dislocation density and microstrain, not crystallite size, determine the F_{2g} FWHM in defective nanorods.
2. Qualitative inspection of the data indicates that ODA concentration has a more pronounced influence than the ethanol/water ratio on aspect ratio, Ce³⁺ content, and bandgap. However, the limited number of synthesis conditions (three levels per factor) prevents a definitive statistical ranking of factor importance; a more comprehensive exploration of the synthesis matrix would be required for robust quantitative prediction.
3. The I_D/I_{F2g} ratio is a sensitive indicator of defect-related disorder associated with oxygen vacancies. Its linear correlation with XPS-derived Ce³⁺ ($R^2 = 0.94$) supports the use of Raman spectroscopy as a non-destructive probe of defect chemistry.
4. Morphology selects properties. Short nanorods (CeO₂-BB) maximize surface area, Ce³⁺ content, and oxygen vacancies—ideal for catalysis. Long rods (CeO₂-MM) offer a narrower bandgap—suitable for photocatalysis.
5. Bandgap engineering requires simultaneous control of size and defects. Quantum confinement and defect-induced narrowing compete, so neither parameter alone predicts E_g . The Urbach energy emerges as a more robust descriptor, as it inherently integrates both structural disorder and defect density.

This integrated approach provides a roadmap for the rational design of rare-earth oxide nanostructures. Future work will evaluate the catalytic activity (e.g., CO oxidation, water–gas shift), ionic conductivity, and gas sensing performance of these morphologies to validate the structure–property–function relationships and guide application-specific design.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/reactions7040060/s1>, Figure S1. Rietveld refinement plots for the CeO₂ samples. Figure S2. Deconvoluted Raman spectra. Figure S3. XPS survey spectra. Figure S4. Statistical analysis of particle dimensions. Figure S5. Supplementary optical analysis. Figure S6. Mechanistic correlations. Figure S7. Comparison between experimental FWHM and Richter–Wang–Ley (RWL) predictions, and correlation between Δ FWHM and microstrain. Table S1. Synthesis parameters and characterization of the CeO₂ nanostructures. Table S2. Descriptive statistics of the morphological parameters of the CeO₂ nanoparticles. Table S3. Comparison of direct and indirect bandgaps. Table S4. One-way ANOVA results for the integrated areas.

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Abbreviations

The following abbreviations are used in this manuscript:

AA	High ODA concentration, high α (CeO ₂ -AA)
AR	Aspect Ratio
ATR	Attenuated Total Reflectance
BB	Low ODA concentration, low α (CeO ₂ -BB)
BET	Brunauer–Emmett–Teller
BJH	Barrett–Joyner–Halenda
C	BET constant
Ce ³⁺	Trivalent cerium
Ce ⁴⁺	Tetravalent cerium
CeO ₂	Cerium oxide (ceria)
CS	Crystallite Size
CV	Coefficient of Variation
D	Defect band (Raman)
DFT	Density Functional Theory
DR	Dubinin–Radushkevich
DRS	Diffuse Reflectance Spectroscopy
E _g	Bandgap energy
E _u	Urbach energy
EtOH	Ethanol
F(R)	Kubelka–Munk function
FT-IR	Fourier-Transform Infrared Spectroscopy
FWHM	Full Width at Half Maximum
H	Kruskal–Wallis statistic
I _D /I _{F2g}	Intensity ratio of defect band to F _{2g} mode
IUPAC	International Union of Pure and Applied Chemistry
M	Intermediate ODA concentration, intermediate α (CeO ₂ -MM)
MM	Intermediate (CeO ₂ -MM)
N ₂	Nitrogen
ODA	Octadecylamine
O _{ads}	Adsorbed oxygen species
O _{def}	Oxygen vacancies/defect oxygen
O _{lat}	Lattice oxygen
p	Statistical significance level
P/P ₀	Relative pressure

PC	Principal Component
PCA	Principal Component Analysis
R	Reflectance
R ²	Coefficient of determination
SA	Surface Area
SD	Standard Deviation
TEM	Transmission Electron Microscopy
UV-Vis	Ultraviolet-Visible
V _P	Total pore volume
XPS	X-ray Photoelectron Spectroscopy
α	Ethanol-to-water volume ratio (EtOH/H ₂ O)

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