Research Article

The Effect of Tartaric Acid and Citric Acid as a Complexing Agent on Defect Structure and Conductivity of Copper Samarium Co-Doped Ceria Prepared by a Sol-Gel Auto-Combustion Method

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Copper samarium co-doped ceria (CSDC) ($\text{Cu}_{0.01}\text{Sm}_{0.19}\text{Ce}_{0.80}\text{O}_{2-\delta}$) nanoparticles were synthesized via a sol-gel auto-combustion of metal nitrates without a complexing agent (DI) and with tartaric acid (TA) or citric acid (CA). The solid oxide formation of CSDC/DI corresponds to the endothermic stage, whereas that of CSDC/TA and CSDC/CA matches the exothermic stage caused by the decomposition of the metal cross-linking and carbon combustion. The cross-linking occurs more extensively in the CA case as more heat is released in CA than in the TA route. The as-synthesized morphology of CSDC/DI reveals both layered structures and small agglomerated particles, whereas CSDC/TA and CSDC/CA show dense xerogel and porous xerogel, respectively. The cubic fluorite structure for calcined CSDCs was confirmed by XRD. From Raman analysis, calcined CSDC/CA has the lowest amount of copper segregation and the highest relative total oxygen vacancy concentration $[V_{\text{O}}^{\bullet\bullet}]_{\text{total}}$, whereas calcined CSDC/DI has the highest amount of copper segregation and the lowest $[V_{\text{O}}^{\bullet\bullet}]_{\text{total}}$. For all samples, copper segregation promotes densification, albeit to varying degrees. The relative densities of CSDC/DI, CSDC/TA, and CSDC/CA pellets are $82.8 \pm 2.4\%$, $95.5 \pm 1.8\%$, and $97.8 \pm 0.9\%$, respectively. The sintered CSDC/DI has the lowest density because some copper segregates and liquid copper in interparticle spaces could evaporate earlier than samples containing a complexing agent, whereas sintered CSDC/CA has the highest density because Cu could slowly diffuse from the Cu-Sm-Ce solid solution to grain boundary regions and then precipitate as CuO. The specific grain boundary conductivity is predominantly influenced by CuO along grain boundaries, which reduces specific grain boundary conductivity and increases the enthalpy of association (ΔH_a) at 250–350°C; however, it rarely impacts total grain boundary conductivity at temperatures higher than 400°C. CSDC/CA has slightly higher total conductivity than CSDC/TA despite having more CuO segregation because it has higher density and $V_{\text{O}}^{\bullet\bullet}$.

1. Introduction

A traditional electrolyte of solid oxide fuel cell (SOFC) is made of yttrium-stabilized zirconia (YSZ), which can efficiently operate at 800–1000°C [1]. Such high operating temperatures come with drawbacks, such as material degradation, a thermal mismatch between fuel cell components, and material incompatibility [2]. Since the oxygen ionic conductivity of ceria-based materials is higher than that of YSZ, ceria-based materials have been recognized as one of the most interesting ionic conductors that operate at intermediate temperatures ranging from 500 to 700°C [1, 3]. To enhance the total conductivity of doped ceria materials, the conductivities of both the grain and the grain boundary must be tuned. Grain conductivity mainly relates to oxygen vacancies and densification, whereas grain boundary conductivity mainly corresponds to oxygen vacancies, densification, grain size, segregation, and impurities [4, 5].

The oxygen vacancies ($V_{\text{O}}^{\bullet\bullet}$) were increased by doping ceria materials with rare-earth (RE) cations (Gd^{3+} , Sm^{3+} , Nd^{3+} , etc.) [6–9]. The formation of $V_{\text{O}}^{\bullet\bullet}$ can be described by the Kröger–Vink notation as follows:

The $V_{\text{O}}^{\bullet\bullet}$ is responsible for ionic conductivity because the oxygen ion (O^{2-}) transport through $V_{\text{O}}^{\bullet\bullet}$ in the ceria lattice by a hopping mechanism within a grain region and then O^{2-} ion will move along or across the grain boundary region [10, 11]. The $V_{\text{O}}^{\bullet\bullet}$ increases with increasing dopant concentration until it reaches an optimal dopant concentration. Anjaneya et al. [4] reported that 20 mol% Sm doped ceria (20SDC) has the highest total conductivity ($\sim 6 \times 10^{-5}$ S/cm at 500°C) and the lowest E_a (0.84 eV) value, as compared to 10SDC ($\sim 3 \times 10^{-5}$ S/cm, 0.87 eV) and 30SDC ($\sim 3 \times 10^{-6}$ S/cm, 1.08 eV). The lowest total conductivity was observed for 30SDC due to an increase in the association of defect (Sm_{Ce}' ; $V_{\text{O}}^{\bullet\bullet}$) complex and impurity phases such as SiO_2 and Sm_2O_3 , resulting in decreased oxygen ion mobility across grain and grain boundaries, respectively. In addition, the conductivity of 10SDC is lower than that of 20SDC because 10SDC has a lower $V_{\text{O}}^{\bullet\bullet}$ and its vacancy sites are further apart, making it difficult for oxygen ions to migrate effectively.

The processing methods affect both grain and grain boundary conductivity [3, 12]. For example, Cioateră et al. [3] compared Gd/Sm co-doped ceria synthesized using Pechini and modified Pechini methods (added Triton X-100 as a surfactant). They reported that using Triton X-100 increased bulk ionic conductivity by preventing the formation of defect complex clusters during sintering. This effect also increases $V_{\text{O}}^{\bullet\bullet}$ even in the space-charge layers, which leads to an increase in grain-boundary conductivity. Kim et al. [12] prepared the aliovalent (Gd^{3+} , Sm^{3+} , and Nd^{3+}) doped ceria with various dopant contents and various preparation methods, including coprecipitation, combustion, solid-state, and hydrothermal methods. Among these methods, the sample obtained from the combustion synthesis has the highest grain and grain boundary conductivities because it has the highest density due to its porous spongy structure made from connected thin-flake

nanocrystallite. Moreover, the grain boundary conductivity of the sample from the combustion method is the highest, which could be due to the fewer impurities. Arabaci and Serin [13] prepared SDC by the Pechini method as compared to the cellulose template method, both of which were sintered at 1400°C. They found that the sample from the cellulose template method has higher total ionic conductivity (0.0342 S/cm at 750°C) than that from the Pechini method (0.0302 S/cm) due to the larger grain sizes and higher density. Moreover, the cellulose template method produces a sample with lower activation energy (E_a) at all temperatures, which could be attributed to high $V_{\text{O}}^{\bullet\bullet}$ diffusion. Khakpour et al. [14] studied the effect of sintering temperature (1300 and 1450°C) and dopant concentration (20SDC and 30SDC) on the sample conductivities. There are no significant changes in grain conductivity with different sintering temperatures or grain sizes. However, grain boundary conductivity decreases with increasing sintering temperature/grain sizes. Moreover, the higher dopant concentration increases grain conductivity by increasing $V_{\text{O}}^{\bullet\bullet}$, and it can also increase grain boundary conductivity due to the scavenging of SiO_2 by the Sm_2O_3 segregation. Also, Pérez-Coll et al. [5] reported that grain and grain boundary conductivities increase with increasing densification. However, grain and grain boundary conductivities only slightly increase when the relative densities are above 91.9% and 93.9%, respectively.

The sol-gel auto-combustion method, also known as sol-gel combustion or modified sol-gel method [15–17], is widely used due to simple preparation, short time-to-product, low cost, higher homogeneity, and fine crystal size with high surface areas in the resulting materials [17, 18]. The sol-gel combustion method includes precursors and a complexing agent with/without additional fuels. Note that complexing agents themselves also function as fuel. The different complexing agents in the sol-gel combustion method could impact synthesized materials in terms of purity, homogeneity, and surface area [19]. The complexing agents widely used in sol-gel combustion mainly contain a carboxylic group such as tartaric acid (TA), citric acid (CA), oxalic acid, etc., or a hydroxyl group such as ethylene glycol (EG), glycerol (GL), etc. Notably, EG was commonly used with carboxylic complexing agents to improve complexing capabilities [20, 21]. Nonetheless, the doped ceria could also be prepared by a single complexing agent. As demonstrated by Mahata et al. [22], GDC nanoparticles were synthesized by the sol-gel combustion method using CA. Furthermore, it was found that the sample pellets sintered at 1250°C achieved 94–97% density. Note that such a low sintering temperature was due to the addition of a polyvinyl alcohol (PVA) binder as a sintering aid. However, the conductivity of the samples was not reported. Another case was reported by Accardo et al. [18] who also prepared GDC powders by sol-gel combustion method using only CA, and their samples were sintered at 1500°C. Their conductivity of 20GDC measured at 600°C is 0.19 S.cm⁻¹, which is higher than that of 10GDC (0.01 S.cm⁻¹) due to higher densification. The effect of different complexing agents on the electrical conductivity of GDC was reported by Zarkov et al. [1]. A complexing agent

in comparison was TA, ethylene glycol (EG), or glycerol (GL), each of which was added to mixed metal nitrate solution. Their samples were sintered at 1300°C. It was found that the sample from the GL route has the maximum conductivity (0.0037 S/cm) due to its highest pellet density. For an additional body of knowledge, TA should be compared to CA because CA also has functional groups similar to TA but differs in molecular structure and the number of coordination ligands.

To increase densification, high sintering temperatures (such as 1300–1650°C) were used to obtain RE-doped ceria materials. If no sintering aids are used and sintering is conducted at high temperatures, this leads to high manufacturing costs, segregation of defect clusters, failure of co-firing with the cathode supported electrode, and reduction of Ce^{4+} to Ce^{3+} [23, 24]. Moreover, the reduction of doped ceria materials at high temperatures as well as low oxygen partial pressure results in mixed ionic and electronic conductivities (MIEC) [25]. The strategies to reduce sintering temperature have been widely investigated such as tuning particle size/shape and adding the sintering aids [20, 26]. The sintering aids with low melting temperatures, such as Cu [20, 25], Li [27], Sr [28], and Zn [29], have been proposed to reduce the sintering temperature. Among sintering aids, copper is the most promising candidate as it is inexpensive; moreover, copper metal or copper oxide nanoparticles (which may coexist with copper) have low melting temperatures that promote the effect of liquid-phase sintering [30], resulting in the reduction of sintering temperatures down to 900–1100°C [20, 25]. High grain mobility during liquid-phase sintering allows grains to rearrange, merge, and then coarsen at lower temperatures. It was also reported that a ternary phase, $\text{Gd}_2\text{O}_3\text{-CeO}_2\text{-CuO}$, could also form and contribute to the sintering process [25]. To date, there have not been many studies involving Cu/Sm co-doped ceria (Cu-SDC) prepared by the sol-gel auto-combustion method. Toor and Croiset [25] produced Cu-20SDC powders with the copper content of 0.1, 0.5, 1.0, 3.0, and 5.0 mol% by the sol-gel combustion method using the only glycine as a complexing agent/fuel. Adding Cu content below 1 mol% results in a low CuO amount at the grain boundaries, which leads to a high value of grain boundary conductivity at low temperatures. Their total conductivities of 0.5Cu-20SDC and 1Cu-20SDC are ~ 0.007 and $\sim 0.006 \text{ S}\cdot\text{cm}^{-1}$ at 600°C, respectively. Lü et al. [31] and Dong et al. [15] prepared 1Cu-20SDC by the sol-gel combustion method with PVA as a complexing agent/fuel. They observed that the total conductivities are 0.0146 and $0.0154 \text{ S}\cdot\text{cm}^{-1}$ at 600°C, respectively.

This study examined the effects of TA and CA used as a single complexing agent for preparing $\text{Cu}_{0.01}\text{Sm}_{0.19}\text{Ce}_{0.80}\text{O}_{1.90}$, which could reveal additional useful information, particularly changes in thermal behaviors, as-synthesized morphologies, densities, $V_{\text{O}}^{\bullet\bullet}$, segregations, and electrical conductivities. Moreover, CSDC powder without additional complexing agents/fuels has never been reported.

2. Experimental

2.1. Powder Synthesis. The composition of CSDC powders in this work was $\text{Cu}_{0.01}\text{Sm}_{0.19}\text{Ce}_{0.80}\text{O}_{1.90}$, which was synthesized by the sol-gel auto-combustion method via three

different routes. Among these were the use of pure de-ionized water (CSDC/DI) as a reference sample and an additional complexing agent, either L-(+)-tartaric acid (CSDC/TA) or citric acid (CSDC/CA). Metal nitrate precursors included $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (99.9%, Sigma-Aldrich), $\text{Sm}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (99.9%, Sigma-Aldrich), and $\text{Cu}(\text{NO}_3)_2$ (99.9%, Sigma-Aldrich). A complexing agent, either tartaric acid (TA, 99.9%, Sigma-Aldrich) or citric acid (CA, 99.9%, Sigma-Aldrich) was used. All metal nitrates were dissolved in de-ionized water at a total concentration of 0.1 M. The mixed metal nitrate solution is CSDC/DI. For CSDC/TA or CSDC/CA, TA or CA was added to the mixed metal nitrate solution at a molar ratio of metals: complexing agent of 1 : 1. After being thoroughly dissolved, each mixed solution was heated to 80°C and continuously stirred until the yellow gel was formed. Each gelled samples was heated in a muffle furnace at 300°C. Then, the as-synthesized powder was transferred into a crucible and calcined at 800°C for 3 h. The calcined powder was ground by dry ball milling for 3 h using zirconia balls with a diameter of 3 mm.

2.2. Pellet Preparation. Each calcined CSDC powder with the weight of $0.5000 \pm 0.0005 \text{ g}$ was subjected to a uniaxial compression of 5 MPa by using a hydraulic press. The green CSDCs pellets with 13 mm diameter were sintered at 1100°C in a muffle furnace at a heating rate of 2°C/min, with a holding time of 3 h and then cooled to 500°C at a rate of 10°C/min. After reaching 500°C, the furnace was shut down and allowed to cool to room temperature. A summary of sample preparation steps is shown in Figure 1.

2.3. Characterization. The resulting gel samples were analyzed by using simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (TGA/DSC1, Mettler-Toledo, Switzerland) from room temperature to 1100°C at a constant heating rate of 10°C/min with air-zero flow rates of 20 ml/min. The reaction enthalpy can be determined by integrating the area of the reaction peak. Scanning electron microscope (SEM) (SNE: 4500-M, SEC, South Korea) was used to characterize the morphology of the as-synthesized samples and sintered pellets. The calcined CSDC powders were characterized using X-ray diffraction (XRD) (X'Pert3, Malvern Panalytical, USA) with a 2θ scan range of 20–90°, Fourier transform infrared spectroscopy (FT-IR) (TENSOR27, Bruker, USA) over a range of 4000–600 cm^{-1} , Raman spectroscopy (T64000 Triple monochromator, JOBIN YVON HORIBA, France) with a wavelength of 532 nm, high-resolution transmission electron microscope (HRTEM) (TecnaïTM G2 20, FEI, USA and X-ray photoelectron spectroscopy (XPS)) (AXIS Ultra DLD, Kratos Analytical, UK). In addition, the sintered CSDC powders were assessed in terms of defect structure and chemical composition using Raman spectroscopy and XPS, respectively. The electrical properties of CSDC pellets were estimated from impedance spectroscopy (PAR4000, Princeton Applied Research (PAR), USA) with a scanning range from 4 MHz to 0.1 Hz.

FIGURE 1: Sample preparation steps to obtain sample pellets.

The relative density (r.d.) was calculated from the relationship between bulk density (ρ_m) and theoretical density (ρ_{th}). The theoretical density was calculated using the following equation [15, 31]:

$$\rho_{th} = \frac{4}{N_A a^3} \left[(1 - (x - y))M_{Ce} + xM_{Sm} + yM_{Cu} + \left(2 - \left(\frac{x}{2}\right)\right)M_O \right], \quad (2)$$

where a is a lattice parameter calculated from XRD, N_A is Avogadro's number (6.022×10^{23}), x is Sm content (Sm = 0.19), and y is Cu content (Cu = 0.01). The Archimedes method was used to determine the bulk densities of sintered CSDC pellets.

For conductivity measurement, silver paste (Ag-paste) was painted on both sides of the sample surfaces in a defined area of 0.28 cm^2 and then the painted pellets were dried at 80°C on a hot plate. The Ag-wires were connected on both sides of the Ag-paste. The samples were placed in the holder and heated in a tube furnace at 850°C for 30 min. The conductivities were measured in a high-temperature range from 800°C to 400°C with an increment of 100°C and a low-temperature range from 400°C to 250°C with an increment of 50°C . The total resistivity (ρ_{tot}) was calculated from the combination of grain and grain boundary resistivity ($\rho_{tot} = \rho_g + \rho_{gb}$) and the conductivity was derived from the following equation [15, 31, 32]:

$$\sigma_{tot} = \frac{1}{\rho_{tot}} = \frac{L}{RA}, \quad (3)$$

where σ_{tot} is the total conductivity ($\text{S}\cdot\text{cm}^{-1}$), ρ_{tot} is the total resistivity ($\Omega\cdot\text{cm}$), L is sample thickness (cm), R is resistance

from impedance spectra (Ω), and A is an active area (cm^2). The activation energy (E_a) was determined from the slope of the Arrhenius plot of $\ln(\sigma T)$ versus $1/T$ following equation [8, 31]:

$$\sigma = \frac{\sigma_0}{T} \exp\left(-\frac{E_a}{k_B T}\right), \quad (4)$$

where σ_0 is the preexponential factor, k_B is Boltzmann's constant ($8.617 \times 10^{-5} \text{ eV}\cdot\text{K}^{-1}$), and T is the absolute temperature in Kelvin.

3. Results and Discussion

3.1. Thermal Analysis. The thermal behavior of Cu-Sm-Ce-O synthesized gels was analyzed using simultaneously TGA/DSC. The results described a complexing agent effect on the solid solution formation of the CSDC compound, which may be different. This thermal behavior is related to the energy released during heating the precursor gels, as shown in Figure 2. Differential thermogravimetric (DTG) analysis was used to confirm the mass loss during the various stages in the TGA curve. Interestingly, the decomposition of metal nitrate hydrate is unique for the fact that metal hydroxide can form without any alkaline additives, which was analyzed by the TGA-MS technique [33, 34]. Herein, we also added the DSC technique to confirm the thermal behavior of metal nitrate decomposition. For TGA and DTG curves, the CSDC/DI gel (Figure 2(a)) shows a mass loss of 16.1% in the 1st step over the temperature range of $63\text{--}130^\circ\text{C}$. This is due to the evaporation of water in the gel, which is related to an endothermic peak (i) with heat flow of 623.5 mJ and enthalpy change ($\Delta H = -134.4 \text{ J/g}$) on DSC curves as shown in Figure 2(d). Afterward, the integral area of the 2nd small exothermic peak (ii) corresponding to heat flow of 109.1 mJ ($\Delta H = 23.5 \text{ J/g}$) is observed while the mass loss on the TGA curve slightly decreases. The thermal behavior is possibly caused by the formation of metal nitrate hydroxide compound as well as $\text{M}(\text{OH})_b(\text{NO}_3)_{(z-b)}\cdot\text{H}_2\text{O}_{(a-b-c)}$ and other byproducts including HNO_3 and H_2O . A further mass loss of the 2nd step on the TGA curve is 10.5% ($198\text{--}207^\circ\text{C}$), which corresponds to an endothermic peak (iii) of about 571.1 mJ ($\Delta H = -123.1 \text{ J/g}$) due to decomposition of $\text{M}(\text{OH})_b(\text{NO}_3)_{(z-b)}\cdot\text{H}_2\text{O}_{(a-b-c)}$ to N_xO_y gases (x and $y = 1$ or 2), coordinated water, and oxygen. For the last TGA step, a mass loss of 33.7% ($286\text{--}328^\circ\text{C}$) corresponds to an endothermic peak (iv) of heat flow of 3038.7 mJ ($\Delta H = -654.9 \text{ J/g}$), which can be ascribed to the decomposition of most hydroxides as well as some metal oxide formation.

The TGA/DTG result of CSDC/TA is shown in Figure 2(b). The mass loss of the 1st step is 43.3% ($82\text{--}110^\circ\text{C}$) and the DSC curve (Figure 2(d)) shows two endothermic peaks. The first endothermic peak (i) of about 1353.6 mJ ($\Delta H = -280.8 \text{ J/g}$) is due to the removal of the excess water in the gel. The second endothermic peak (ii) with a heat flow of 217.0 mJ ($\Delta H = -45.0 \text{ J/g}$) results from the removal of coordinated water molecules. A small exothermic peak (iii) at 149°C of about 80.43 mJ ($\Delta H = 16.7 \text{ J/g}$) is possibly caused by the metal-tartrate formation (metal-TA complex) and

FIGURE 2: TGA/DTG curves of sample gel for (a) CSDC/DI, (b) CSDC/TA, (c) CSDC/CA, and (d) DSC curves.

intermolecular complexation of some metal-TA (cross-linking), while the TGA curve still slightly decreases in the temperature range of 139 to 170°C. The cross-linking of the metal-TA complex leads to the formation of an organo-metallic framework as depicted in Figure 3(a). The mass loss of the 2nd step on the TGA curve is 10.6% (175–195°C), which results from the decomposition of the nitrate and organic compounds from some metal-TA complexes. At the same time, the large exothermic peak (iv) with a heat flow of 847.9 mJ ($\Delta H = 175.9$ J/g) is observed in this step. Despite the fact that N_xO_y gases are not combustible, they are a strong oxidizer that increased combustion energy, and the heat release is attributed to the combustion reaction of carbon and O_2 with N_xO_y gases as an accelerant under wet conditions. For the 3rd step on the TGA curve, the mass loss is 12.1% (284–307°C) due to the decomposition of organic residue, remnant nitrate, and most hydroxide. Moreover, this step is accompanied by a weak exothermic peak (v) with a heat flow of 69.0 mJ ($\Delta H = 14.3$ J/g), which may be caused by the combustion of carbon residue and remnant N_xO_y accelerants under drier conditions. The last step on the TGA curve in the temperature range from 326 to 373°C shows a mass loss of 3.9%, and the DSC curve shows a small

endothermic peak (vi) with a heat flow of 179.4 mJ ($\Delta H = -37.2$ J/g). This thermal behavior may be caused by the thermal decomposition of the CSDC compound due to oxidation phenomena of Ce^{3+} to Ce^{4+} , as reported by Ambrozini et al. [35]. This DSC stage, on the other hand, could be associated with the decomposition of some copper hydroxy-carbonate (malachite) into copper oxide, water, and carbon dioxide [36].

For the CSDC/CA gel (Figure 2(c)), the TG/DTG curve shows a mass loss at the 1st step of 37.9% (68–102°C) due to residual water evaporation, which shows an endothermic peak (i) with a heat flow of 2883.0 mJ ($\Delta H = -613.4$ J/g). Afterward, the small endothermic peak (ii) of about 114.9 mJ ($\Delta H = -24.5$ J/g) is observed in the temperature range from 129 to 138°C, while the TGA curve slightly decreases simultaneously due to dehydration of water molecules. The 2nd and 3rd steps on the TGA curve are overlapping due to the partial consecutive losses of metal-CA complex compound [35], which involves 11.3% (139–166°C) and 7.3% mass loss (195–217°C). They are related to the removal of coordinated water molecules and the decomposition of nitrate and an organic compound. Both steps exhibit exothermic behaviors on the DSC curve

FIGURE 3: The possible cross-linking formation of (a) metal-TA and (b) metal-CA compounds. The illustrations are modified from Fajardo et al. [37] and Wu et al. [38].

of CSDC/CA (Figure 2(d)). The first exothermic peak (iii) has a heat flow of about 249.9 mJ ($\Delta H = 53.2$ J/g) which may be caused by metal-citrate formation (metal-CA complex) and metal-CA complex cross-linking. A possible illustration of the metal-CA cross-linkage is shown in Figure 3(b). The 3rd step on TGA curve is related to the exothermic peak with a heat flow of 1124.9 mJ ($\Delta H = 239.4$ J/g), which could be attributed to heat release from the combustion reaction between carbon and O_2 with N_xO_y gas accelerant under wet conditions.

For the final step on the TGA curve, a mass loss of 14.5% is observed in the temperature range from 292 to 319°C due to the decomposition of organic residue, remnant nitrate, and hydroxide, and the release of carbon as well as metal oxide formation, which corresponds to an exothermic peak with a heat flow of 2613.8 mJ ($\Delta H = 556.1$ J/g) and to the combustion reaction between carbon with N_xO_y gas accelerant under dry conditions.

When CSDC/TA gel is compared to CSDC/CA gel, the integral of the exothermic peak (iii) at $\sim 150^\circ\text{C}$ for CSDC/TA is lower than that of CSDC/CA because CSDC/TA has a lower degree of cross-linking than CSDC/CA. This leads to lower heat release at $\sim 200^\circ\text{C}$ on the DSC curve of CSDC/TA and lower combustion temperature, as well. Because TA has a lower cross-linking degree, it releases fewer N_xO_y gases. Moreover, the amount of carbon and oxygen in TA is lower than that of CA, resulting in less combustion energy. The final heat release (v) at $\sim 300^\circ\text{C}$ of CSDC/TA is much lower than that of CSDC/CA at $\sim 325^\circ\text{C}$ due to the lower amount of carbon residue as some carbon in CSDC/TA transforms into carbonate species such as copper hydroxycarbonate (malachite), which exhibits a weak endothermic peak at $\sim 365^\circ\text{C}$.

3.2. FT-IR Analysis. FT-IR was used to confirm the presence of carbon-oxygen residues after calcination. The FT-IR

spectra of calcined CSDCs prepared by DI, TA, and CA routes are presented in Figure 4. All samples show vibration bands at $\sim 3500\text{ cm}^{-1}$, $\sim 1650\text{ cm}^{-1}$, 1500 cm^{-1} , and $\sim 1300\text{ cm}^{-1}$, which are attributed to the O-H stretching of water, O-H stretching, O-C-O stretching, and N-O stretching, respectively [15, 18, 39, 40]. The O-H vibration mode of water molecules is observed due to moisture adsorption or possibly Ce-OH at sample surfaces [41]. Moreover, the O-H vibrational modes come from the amorphous phases of hydroxyl species, such as $\text{Ce}(\text{OH})_3$ and $\text{Ce}(\text{OH})_4$ or $\text{CeO}_2 \cdot 2\text{H}_2\text{O}$ [42]. The probable formations of $\text{Ce}(\text{OH})_3$ and $\text{Ce}(\text{OH})_4$ as well as the derivation of CeO_2 nanoparticles are as follows [43]:

However, the C-O stretching is also observed in calcined CSDC/DI, which results from CO_2 absorption at the particle surfaces from the environment [41]. Moreover, the carbonate groups in the FT-IR spectra may have been caused by the reaction of nitrate and CO_2 (from burning complexing agents) during the combustion stage according to the following reaction [18]:

Moreover, the vibration band at $850\text{--}400\text{ cm}^{-1}$ is the characteristic of Ce-O bonds [18, 44]. Although CSDCs were calcined at 800°C , the FT-IR spectra still show -OH vibration, carbon, and carbonate residues from burnt complexing agents that may be trapped along grain boundaries of nanoparticles during calcination. Notably, the residues of an organic compound can still be detected after calcination at temperatures of up to 1000°C , which has been reported by Kalyk et al. [45].

FIGURE 4: FT-IR spectra of (a) CSDC/DI, (b) CSDC/TA, and (c) CSDC/CA calcined powders.

3.3. Scanning Electron Microscopy (SEM). Figure 5 shows various morphologies of as-synthesized CSDCs that were prepared using three different nitrate precursors: pure DI, or TA complex, or CA complex. The as-synthesized CSDC/DI has both a layered structure (yellow arrow) and small agglomerated particles (green arrow), as shown in Figures 5(a) and 5(b). The layered structure comes from gel drying without combustion, while the observed small particles are generated by mild combustion. However, the form of as-synthesized CSDC/TA (Figures 5(c) and 5(d)) is dense xerogel and porous xerogel for as-synthesized CSDC/CA (Figures 5(e) and 5(f)) because the bubbles in CSDC/CA can be extensively generated and expanded more than those of CSDC/TA during the gas-release stage. CA can stretch more than TA when bubbles enlarge because CA has a higher viscosity. In addition, the CA has a branch structure and more coordination, resulting in more cross-links in the CA route. Moreover, CA has a higher carbon content than TA. Therefore, the as-synthesized CSDC/CA exhibits stronger combustion than the as-synthesized CSDC/TA, which leads to a higher energy release that is confirmed by the DSC result.

3.4. Transmission Electron Microscopy (TEM). TEM was used to characterize the crystallinity and particle sizes of ungrounded samples after the calcination of nanoparticle powders. It was found that geometry of all samples are mostly polyhedral and the particles demonstrate agglomeration as seen in Figures 6(a)–6(c). Because CSDC/DI nanoparticles form more metal hydroxide than CSDC/TA and CSDC/CA nanoparticles, it shows higher agglomeration with lower dispersion than the others. Moreover, TA and CA can form an organometallic complex, which improves metal ion dispersion in solution. In addition, CA has a branched molecule and more coordination ligands, resulting in greater dispersion of nanoparticle sizes than TA. The particle sizes of CSDC samples are shown in Figures 6(d)–6(f), while the histograms in the inserted figures show the particle size distribution. The CSDC/TA and CSDC/CA have greater combustion than CSDC/DI; however, the particles of all

samples are nonuniform in size. Moreover, the formation of organometallic compounds can inhibit nanoparticle agglomeration during the auto-combustion process, as well as increase the degree of cross-linking, which leads to more combustion energy. The average particle sizes of CSDC/DI, CSDC/TA, and CSDC/CA are approximately 35.5 ± 9.9 nm, 35.0 ± 10.3 nm, and 35.2 ± 11.1 nm, respectively. Nevertheless, the average particle sizes are close to one another because only dry suspended nanoparticles were measured using the TEM technique.

The crystallinities of CSDC nanoparticles are estimated by selected area electron diffraction (SAED). The SAED patterns of CSDC nanoparticles are shown in Figures 6(g)–6(i). The CSDC/DI nanoparticles have poor crystallinity as shown in Figure 6(g), which may have been caused by the presence of amorphous phases of hydroxyl species such as $\text{Ce}(\text{OH})_3$ and $\text{Ce}(\text{OH})_4$ or $\text{CeO}_2 \cdot 2\text{H}_2\text{O}$ at the particle surfaces [42], as well as amorphous CuO. This leads to decreased crystallinity. The broad reflection rings of CSDC/TA and CSDC/CA nanoparticles show eight rings that can be ascribed to (111), (200), (220), (311), (222), (400), (331), and (420) [15]. The CSDC/TA and CSDC/CA nanoparticles have higher crystallinity than the CSDC/DI nanoparticles because the complexing agent can produce metal-complexes, which decrease the coordinated -OH, and another reason is the existence of an exothermic behavior, which results in faster metal oxidation. According to TEM analysis, the complexing agents can aid in crystallinity improvement.

3.5. XRD Patterns. The XRD patterns of all calcined CSDCs show an FCC fluorite CeO_2 phase (JCPDS Card No. 00-034-0394) with no detected Sm_2O_3 or CuO, which are typical impurity phases as shown in Figure 7(a). However, it is difficult to identify CuO impurity phase because the level of Cu is lower than the detection limit of the XRD technique [21]. Because the calcined CSDC/CA has the highest peak intensity, it has higher crystallinity than the calcined CSDC/TA and CSDC/DI, which confirms the SEAD data. In addition, the XRD pattern can be used to calculate a lattice parameter by Bragg's relationship. The change in 2θ peak shift and lattice parameters depends on doping efficiency and dopant size. Higher doping efficiency and larger dopant size should lead to a decrease in 2θ peak positions and an increase in lattice parameters. Thus, the substitution of Sm^{3+} into Ce^{4+} sites should increase the lattice parameter and 2θ peaks shift to lower angles because the cationic radius of Sm^{3+} (0.108 nm) is larger than Ce^{4+} (0.097 nm) [8]. Apart from the dopant effect, the complexing agents also have a clear influence on the shift of 2θ peaks in calcined SDC powders without copper ($\text{SDC/DI} < \text{SDC/TA} < \text{SDC/CA}$), as shown in Figure S1. As a result, the complexing agent affects the solubility of Sm in ceria. When copper is added to SDCs, the trend in the 2θ peak shift is uncertain, except for the (220) peak, as shown in Figure S2. The lattice parameters of calcined CSDC powders are averaged from all peak positions, as shown in Figure 7(b). The average lattice parameters of calcined CSDC/TA and CSDC/CA are slightly higher than that of calcined CSDC/DI. When calcined CSDC/CA is compared to calcined CSDC/TA, the

FIGURE 5: As-synthesized powder morphology at 1k magnification for (a) CSDC/DI, (c) CSDC/TA, and (e) CSDC/CA, and 5k magnification for (b) CSDC/DI, (d) CSDC/TA, and (f) CSDC/CA.

average lattice parameter of calcined CSDC/CA is close to that of CSDC/TA, which may be due to more substitution of Cu^+ (0.074 nm) and/or Cu^{2+} (0.071 nm) into Ce^{4+} [46]. The crystallite sizes (D) are estimated from Scherrer's equation as follows [8, 47]:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (7)$$

where λ is X-ray wavelength ($\text{Cu K}\alpha_1 = 1.5418 \text{ \AA}$), θ is the Bragg diffraction angle of peak max, and β is full-width half max (FWHM) in radians. The average crystallite sizes were calculated from all peak locations and it was found that CSDC/DI (18.65 nm) and CSDC/TA (16.72 nm) are not different, while the crystallite size of calcined CSDC/CA (34.29 nm) is similar to that seen in the TEM result. Alternately, the crystallite sizes at (111) peak are in the following order: CSDC/DI

(21.89 nm) > CSDC/TA (23.88 nm) > CSDC/CA (37.53 nm). The calcined CSDC/CA's crystallite size derived from (111) is the highest due to its strongest exothermic reaction, whereas the crystallite size of calcined CSDC/TA is slightly higher than that of calcined CSDC/DI because the calcined CSDC/TA has less hydroxide formation due to the metal-TA complexing and it also exhibits exothermic reaction.

3.6. Visible Raman Spectroscopy. Visible Raman spectroscopy is a highly sensitive technique that can be used to analyze the local structure of nanomaterials, which relates to both bulk and surface defects [48]. Thus, Raman spectroscopy can detect $V_{\text{O}}^{\bullet}$ and distinguish the F-structure (fluorite of CeO_2) and C-structure (cubic of Sm_2O_3) [49, 50]. The Raman spectra of calcined and sintered CSDCs shown in Figure 8 exhibit main peaks at around 250, 460, 550, and

FIGURE 6: The HRTEM images (a–c), high magnification of HRTEM images with particle size distribution histograms (d–f), and SAED patterns (g–i). The left side represents CSDC/DI nanoparticles, the center represents CSDC/TA nanoparticles, and the right side represents CSDC/CA nanoparticles.

600 cm^{-1} and the weak intensity band at $\sim 350\text{ cm}^{-1}$. The strong peak at $\sim 460\text{ cm}^{-1}$ is related to the F_{2g} symmetrical vibrational mode of the Ce–O bond in 8-fold coordination within the CeO_2 cubic fluorite structure [50, 51]. However, the replacement of Ce^{4+} with Sm^{3+} and Cu^{2+} cations generates the $V_{\text{O}}^{\bullet\bullet}$ and induces the vibration peaks in Raman spectra at ~ 250 and $\sim 550\text{ cm}^{-1}$ which relate to the interaction between $V_{\text{O}}^{\bullet\bullet}$ and six next-nearest neighbor oxygen

atoms and the extrinsic $V_{\text{O}}^{\bullet\bullet}$, respectively [50–52]. Moreover, the Raman spectra in the range of $520\text{--}650\text{ cm}^{-1}$ (D mode) exhibit three deconvolutions, as shown in Figures 8(a) and 8(b). D1 ($\sim 550\text{ cm}^{-1}$) is extrinsic $V_{\text{O}}^{\bullet\bullet}$ [53, 54]. D2 ($\sim 600\text{ cm}^{-1}$) includes intrinsic $V_{\text{O}}^{\bullet\bullet}$ [49, 55–57] or $V_{\text{O}}^{\bullet\bullet}$ dealing with Frenkel (anion pair) defects [48, 53, 58]. D3 ($\sim 630\text{ cm}^{-1}$) is related to extrinsic defects or the oxidized site of dopant cations without any $V_{\text{O}}^{\bullet\bullet}$ (REO_8 -type), which was

FIGURE 7: (a) XRD patterns of calcined CSDCs and (b) lattice parameters and crystallite size.

FIGURE 8: Raman spectra of (a) calcined CSDCs and (b) sintered CSDCs. (c, d) Normalized intensities of calcined and sintered CSDCs, respectively. The inserted pictures in (a) and (b) specifically show D bands, whereas the inserted pictures in (c) and (d) represent the F_{2g} Raman shift.

assigned to SmO_8 -type complex in this case [48]. In addition, a very weak Raman band at $\sim 350 \text{ cm}^{-1}$ in calcined and sintered CSDCs is assigned to copper segregation such as CuO [59] could overlap with the C-structured Sm_2O_3 ($\sim 370 \text{ cm}^{-1}$) [56].

Because the XRD peak shift cannot clearly explain the dopant solubility into the ceria lattice for calcined CSDCs, Raman spectroscopy is analyzed and used to extract solubility information based on F_{2g} characteristics (intensity, peak shift, broadening, and shoulders), $V_O^{\bullet\bullet}$, and segregation. The F_{2g} intensities of calcined and sintered CSDCs, as shown in Figures 8(a) and 8(b), are in the following order: CSDC/DI > CSDC/TA > CSDC/CA. When TA or CA was added, the F_{2g} intensity decreases because there are fewer Ce-O symmetry vibrations and an increase in lattice disorder [52] due to the improvement of Sm and Cu substitution. To confirm the efficacy of TA or CA in doping, the F_{2g} shift should be analyzed. Because of the radius of $\text{Sm}^{3+} > \text{Ce}^{4+} > \text{Cu}^{2+}$, the replacement of Ce^{4+} with Sm^{3+} causes F_{2g} to shift to lower wavenumber (red-shift), resulting in lattice expansion, whereas Cu^{2+} substitution causes F_{2g} to shift to higher wavenumber (blue-shift), resulting in lattice contraction. However, the shift of F_{2g} induced by the Cu^{2+} ions is insignificant because of the low Cu concentration of only 1 mol%. The F_{2g} peak positions of calcined and sintered CSDCs follow the same trend: CSDC/CA < CSDC/TA < CSDC/DI. Moreover, the sintered CSDCs exhibit a slight red-shift in F_{2g} compared to the calcined CSDCs due to the removal of Cu and hydroxide species (especially CSDC/DI). The interpretation of F_{2g} intensity and peak shift confirms that the addition of TA and CA affects doping efficiency. The CA could facilitate more metal-CA formation than metal-TA, so the substitution of Sm and Cu into ceria can be the best in the CA case.

The intensities of all Raman spectra have been normalized to compare the broadening of F_{2g} . The broadening of F_{2g} is caused by the decrease in lattice symmetry [58] and/or the decrease in crystal sizes as well as an increase in defects [60]. Moreover, the left shoulder of F_{2g} at $\sim 404 \text{ cm}^{-1}$ is related to lattice distortion [48], whereas the right shoulder of F_{2g} is S-mode ($\sim 470 \text{ cm}^{-1}$) which could be ascribed to a surface mode appearing in very small crystallites like $\text{CeO}_{2-\delta}$ [61] or relates to the nonequivalence of cation-O bonds in doped or reduced ceria [62]. From Figure 8(c), the S-mode broadening of calcined CSDC/CA and CSDC/TA are higher than that of calcined CSDC/DI, indicating the increase of Sm and/or Cu solubility in ceria. However, the S-mode of sintered CSDCs decreases (Figure 8(d)) with increasing particle size and oxygen intake, which results in the improvement of lattice ordering [61].

From Figure 8, the calcined and sintered CSDCs have a very weak Raman band at $\sim 350 \text{ cm}^{-1}$, which may be attributed to the Raman band of Cu^{2+} ions segregating such as CuO . Rashad et al. [59] reported the Raman bands of CuO shown at 282, 330, and 616 cm^{-1} . It is worth noting that the Raman band at 616 cm^{-1} cannot be detected because it is situated within the D2 band. The calcined CSDC/DI has more CuO segregation because of the dehydration of Cu(OH)_2 and partial transformation into CuO when the

temperature is higher than 70°C [63]. It is possible that Cu^{2+} in TA and CA routes is not only in the form of CuO but also copper carbonate (CuCO_3) due to reaction between carbon and Cu^{2+} during the calcination process since the C-O bond is observed in the FT-IR. In addition, a peak of the copper segregation phase at $\sim 354 \text{ cm}^{-1}$ may overlap with that of Sm_2O_3 ($\sim 370 \text{ cm}^{-1}$), if the C-structured Sm_2O_3 segregate exists.

The extrinsic $V_O^{\bullet\bullet}$ (D1) is generated from the substitution of Ce^{4+} with Sm^{3+} and Cu^{2+} and/or Cu^+ (equations (8) and (9)), whereas intrinsic $V_O^{\bullet\bullet}$ (D2) are generated from the partial reduction of Ce^{4+} to Ce^{3+} (equation (10)) due to high temperature/low oxygen partial pressure [50, 52], non-stoichiometry of ceria [57, 64], and redox reaction of $\text{Cu}^+ + \text{Ce}^{4+} \leftrightarrow \text{Cu}^{2+} + \text{Ce}^{3+}$ above 450°C [65], which leads to lattice expansion. In addition, the D2 peak can also be assigned to Frenkel-related defects (equations (11) and (12)). The formation of extrinsic $V_O^{\bullet\bullet}$ (ext. $V_O^{\bullet\bullet}$), intrinsic $V_O^{\bullet\bullet}$ (int. $V_O^{\bullet\bullet}$), and Frenkel defects written in Kröger-Vink notations were summarized as follows [57, 64]:

Extrinsic oxygen vacancy from Sm^{3+} :

Extrinsic oxygen vacancy from Cu ions:

Intrinsic oxygen vacancy and Frenkel defect:

The relative oxygen vacancy concentration, $[V_O^{\bullet\bullet}]$, is estimated from the area ratio of ext. $V_O^{\bullet\bullet}$ at $\sim 550 \text{ cm}^{-1}$ or $V_O^{\bullet\bullet}$. $V_O^{\bullet\bullet}$ at $\sim 600 \text{ cm}^{-1}$ to F_{2g} peak [48], which is calculated after Gaussian fitting [54, 58]. Besides, the relative concentration of SmO_8 , $[\text{SmO}_8]$, is calculated from $A_{\text{SmO}_8}/A_{F_{2g}}$. Note that F_{2g} areas of calcined and sintered CSDCs include the area of F_{2g} shoulders (~ 450 and $\sim 470 \text{ cm}^{-1}$). The relative concentrations of defects are investigated by comparing these area ratios, as shown in Figure 9.

The relative concentration of extrinsic $V_O^{\bullet\bullet}$, $[V_O^{\bullet\bullet}]_{\text{ext.}}$, shown in Figure 9(a) is increased in both calcined and sintered CSDCs following CSDC/DI < CSDC/TA < CSDC/CA. The increase of $[V_O^{\bullet\bullet}]_{\text{ext.}}$ for calcined CSDCs comes with the improved incorporation of Sm^{3+} and Cu ions into the ceria host lattice. Nevertheless, copper and Sm_2O_3 peaks are observed in both calcined and sintered CSDCs even though TA or CA is added, as shown in Figure S3. Since the ratio of Sm_2O_3 to F_{2g} peak (Figure S4(a)) is small, the Sm_2O_3 may segregate in the form of nanodomains phase rather than microdomains phase. The C-structure of Sm_2O_3 nanodomains was also reported for the Sm concentration of

FIGURE 9: The relative concentration of (a) extrinsic $V_O^{\bullet\bullet}$, (b) intrinsic $V_O^{\bullet\bullet}$, (c) total $V_O^{\bullet\bullet}$, and (d) SmO₈-type complex.

~20 mol%, which was detected by μ -Raman spectroscopy [66]. Moreover, the earlier work from Artini et al. [56] showed the obvious segregation of C-structured Sm₂O₃ as determined by μ -Raman spectroscopy and Synchrotron X-ray Diffraction when the Sm³⁺ concentration was 30 mol %. Comparing the $[V_O^{\bullet\bullet}]_{ext.}$ of calcined and sintered CSDCs, the sintered CSDCs have a lower $[V_O^{\bullet\bullet}]_{ext.}$ than calcined ones due to oxygen uptake during the sintering process [61].

The relative concentration of intrinsic $V_O^{\bullet\bullet}$, $[V_O^{\bullet\bullet}]_{int.}$, is shown in Figure 9(b). The $[V_O^{\bullet\bullet}]_{int.}$ is increased due to increasing nonstoichiometry, which results from the decrease in the nanoparticle size [67]. In the presence of Cu²⁺, the effect of the redox reaction of $Cu^+ + Ce^{4+} \rightarrow Cu^{2+} + Ce^{3+}$ could produce Cu²⁺ which exists in three forms, including CuO or Cu-Sm-Ce solid solution, all of which can coexist. Comparing calcined CSDC/TA with calcined CSDC/CA, the calcined CSDC/TA has the higher $[V_O^{\bullet\bullet}]_{int.}$ because it has smaller crystallite sizes according to the XRD result

(Figure 7(b)). The TA route shows a smaller crystallite size because crystal growth is impeded by the presence of CuO and CuCO₃. More of these extra phases appear in the TA route than in the CA route because TA contains fewer coordination ligands, resulting in more free metal ions that readily transform into copper segregation, as shown in Figure S4(b). This implies that TA is not as good as CA in promoting the formation of the Cu-Sm-Ce solid solution. However, calcined CSDC/DI has the highest concentration of copper segregation, which implies the least amount of the formation of Cu-Sm-Ce solid solution. Comparing calcined with sintered CSDCs, the $[V_O^{\bullet\bullet}]_{int.}$ of sintered CSDCs are lower due to the partial oxidation of Ce³⁺ to Ce⁴⁺ [68]. Moreover, the increase in $[V_O^{\bullet\bullet}]$ corresponds to carbon adsorption and CO gas, which could generate $V_O^{\bullet\bullet}$, while H₂O removes it [69, 70]. These phenomena could increase the $[V_O^{\bullet\bullet}]_{int.}$ of calcined CSDC/TA because the as-synthesized CSDC/TA has a dense xerogel structure which could

trap carbon. The relative concentration of total $V_{\text{O}}^{\bullet\bullet}$, $[V_{\text{O}}^{\bullet\bullet}]_{\text{total}}$, is the sum of $[V_{\text{O}}^{\bullet\bullet}]_{\text{ext.}}$ and $[V_{\text{O}}^{\bullet\bullet}]_{\text{int.}}$, as shown in Figure 9(c). The $[V_{\text{O}}^{\bullet\bullet}]_{\text{total}}$ of calcined CSDCs is as follows: CSDC/DI < CSDC/CA < CSDC/TA, whereas sintered CSDCs are as follows: CSDC/DI < CSDC/TA < CSDC/CA. The largest difference in $[V_{\text{O}}^{\bullet\bullet}]_{\text{total}}$ between calcined and sintered CSDCs is observed for CSDC/TA because the calcined CSDC/TA has a high $[V_{\text{O}}^{\bullet\bullet}]_{\text{int.}}$.

Another type of segregate mentioned in literature is the SmO_8 -type complex, which causes the presence of microdomains in the microstructure with a predominant metastable C-type phase [47]. In this study, the relative concentration of the SmO_8 -type complex, $[\text{SmO}_8]$, is shown in Figure 9(d). The $[\text{SmO}_8]$ of calcined CSDCs are in the following order; CSDC/DI >> CSDC/TA > CSDC/CA. The calcined CSDC/CA has less $[\text{SmO}_8]$ than calcined CSDC/TA because CA can improve the solubility of Sm^{3+} ions. Remarkably, the $[\text{SmO}_8]$ of sintered CSDCs in DI and TA routes is lower than that of calcined CSDCs due to the increase in the lattice ordering level, implying that the metastable SmO_8 -type complex could be transformed into a more stable $(2\text{Sm}_{\text{Ce}}^{\text{I}}:V_{\text{O}}^{\bullet\bullet})$ complex with increasing temperature. Note that the $[\text{SmO}_8]$ of sintered CSDC/DI (3.0×10^{-3}) and CSDC/TA (2.8×10^{-4}) are small, which is similar to the $[\text{Sm}_2\text{O}_3]$ case, so we consider the segregated SmO_8 as a part of the nanodomains. However, the sintered CSDC/CA shows a twofold increase in $[\text{SmO}_8]$ as compared to the calcined CSDC/CA (from 0.0048 to 0.01), which may be caused by the diffusion of Cu ions from Cu-Sm-Ce solid solution into CuO along grain boundary regions during the sintering process. The possible explanation is that a redox reaction: $\text{Cu}^+ + \text{Ce}^{4+} \leftrightarrow \text{Cu}^{2+} + \text{Ce}^{3+}$ has occurred, which corresponds to the reduction of Ce^{4+} , resulting in the increasing of $[V_{\text{O}}^{\bullet\bullet}]_{\text{int.}}$ (Figure 9(b)), as well as CuO segregation (Figure S4(a)) for sintered CSDC/CA. However, CuO amount in sintered CSDC/CA is closed to those in other samples because a certain degree of CuO is evaporated

during the sintering process, thereby increasing the metastable SmO_8 (as well as Sm_2O_3 nanodomains) of sintered CSDC/CA.

3.7. XPS Spectra. The XPS was a technique used to evaluate the surface chemical composition and oxidation states of the materials. Since Raman spectroscopy was used to characterize the materials at a deeper depth than XPS, the trend of Ce^{3+} and Cu ion concentration from XPS may be different from that of the Raman results. Moreover, the XPS technique was measured under ultra-high vacuum which induced reduction conditions so that the Ce^{3+} content can be overestimated. Cerium has two oxidation states, Ce^{3+} and Ce^{4+} , which can be observed in high-resolution Ce3d spectra extending from 875 to 925 eV. The detected Ce^{3+} can exist in the $\text{Ce}^{3+}-V_{\text{O}}^{\bullet\bullet}$ and Ce_2O_3 and/or $\text{Ce}(\text{OH})_3$ forms. The formation of $\text{Ce}^{3+}-V_{\text{O}}^{\bullet\bullet}$ is not only generated by external doping but also created under high temperature and/or low partial oxygen pressure. The coexistence of Ce^{3+} and Ce^{4+} as present in Figures 10(a) and 10(b) is confirmed by the high-resolution Ce3d XPS spectra of calcined and sintered CSDCs. The different peaks of Ce $d_{5/2}$ and Ce $d_{3/2}$ spin-orbital components are attributed to v and u [71]. In addition, the v , v' , v'' , u^0 , u'' , and u''' refer to the Ce^{4+} final state, which is ascribed to $\text{Ce}^{4+}-3d^94f^1\text{O}2p^4$ for the doublet v/u , $\text{Ce}^{4+}-3d^94f^1\text{O}2p^5$ for the doublet v''/u'' , and $\text{Ce}^{4+}-3d^94f^1\text{O}2p^6$ for the doublet v'''/u''' , whereas u''' is not observed in pure CeO_2 [72]. Doublet v^0 , v' , u^0 , and u' refer to the Ce^{3+} final state and the binding energy doublet v'/u' , and v^0/u^0 corresponds to $\text{Ce}^{3+}-3d^94f^1\text{O}2p^6$ and $\text{Ce}^{3+}-3d^94f^1\text{O}2p^5$, respectively [73]. However, v^0 and u^0 could not be fitted because they have such low intensities.

The relative concentration of Ce^{3+} , $[\text{Ce}^{3+}]$, is calculated from the ratio of the total area of Ce^{3+} and that of Ce^{4+} as follows [57]:

$$[\text{Ce}^{3+}] = \frac{A_{\text{Ce}^{3+}}}{A_{\text{Ce}^{3+}} + A_{\text{Ce}^{4+}}} = \frac{(v^0 + v' + u^0 + u')}{(v^0 + v' + u^0 + u') + (v + v'' + v''' + u + u'' + u''')}, \quad (13)$$

where $A_{\text{Ce}^{3+}}$ is the total area under the Ce^{3+} peaks and $A_{\text{Ce}^{4+}}$ is the total area under the Ce^{4+} peaks.

The $[\text{Ce}^{3+}]$ values of calcined CSDC/DI, CSDC/TA, and CSDC/CA are 25.70%, 17.95%, and 16.23%, respectively. The $[\text{Ce}^{3+}]$ of calcined CSDCs as shown in Table 1 is decreased when adding TA or CA because Sm^{3+} and Cu ions can substitute into Ce^{4+} sites, which leads to the formation of Cu-Sm-Ce solid solution. Since CA has a high carbon source, the oxidation reaction of $\text{Ce}^{3+} + \text{Cu}^{2+} \rightarrow \text{Ce}^{4+} + \text{Cu}^+$ during CO release [65] could occur in the CA route more than other routes, which leads to decreasing $[\text{Ce}^{3+}]$ value. However, the $V_{\text{O}}^{\bullet\bullet}$ at the particle surface could be depleted by CO_2 adsorption from the atmosphere. Chang et al. [69] reported that the

reaction involving CO_2 reduction by $\text{CeO}_{2-\delta}$ could occur without heat or with a low CO_2 partial pressure, and that if a catalyst metal such as Cu is present on Ce^{3+} , dissociation of CO_2 to CO will occur rapidly. Note that the Ce^{3+} from the XPS result is not only related to the reduction of Ce^{4+} to Ce^{3+} from cation replacement but also the segregation of Ce_2O_3 and/or $\text{Ce}(\text{OH})_3$ at the surface. If interpretation is based on the Ce^{3+} segregation, then CA is confirmed to be a better complexing agent than TA as CA induces the least segregation.

For sintered CSDCs, there are no significant differences in $[\text{Ce}^{3+}]$ values. The values of $[\text{Ce}^{3+}]$ are 20.57%, 21.85%, and 20.26% for CSDC/DI, CSDC/TA, and CSDC/CA, respectively. When calcined and sintered CSDCs are

FIGURE 10: High-resolution XPS spectra of (a) Ce3d for calcined powders, (b) Ce3d for sintered powders, (c) O1s for calcined powders, and (d) O1s for sintered powders.

TABLE 1: The summaries of calculated Ce^{3+} concentration, $\text{O}_{1s}\text{Ce}^{3+}$, stoichiometry (x), and actual stoichiometry (x') for calcined and sintered CSDCs.

Samples	$[\text{Ce}^{3+}]$	$[\text{O}^{2-}]\text{Ce}^{3+}$	x (equation (13))	x' (equation (14))
<i>Calcined</i>				
CSDC/DI	0.2570	0.3273	1.8715	1.8357
CSDC/TA	0.1795	0.2603	1.9102	1.8691
CSDC/CA	0.1623	0.1986	1.9188	1.6517
<i>Sintered</i>				
CSDC/DI	0.2057	0.1832	1.8971	2.0926
CSDC/TA	0.2185	0.1411	1.8908	1.4539
CSDC/CA	0.2026	0.1426	1.8987	2.2351

compared, the $[\text{Ce}^{3+}]$ value of sintered CSDC/DI is found to be lower than that of calcined CSDC/DI due to the partial transformation of $\text{Ce}(\text{OH})_3$ to CeO_2 . However, the $[\text{Ce}^{3+}]$ values of sintered CSDC/TA and CSDC/CA are more than those of calcined ones because of the reduction of Ce^{4+} to Ce^{3+} and the oxidation of Cu^+ to Cu^{2+} at 1100°C . The Ce^{3+} of

sintered CSDC/TA and CSDC/CA concentrates at the surface because the Cu-O and Ce-O bonds in the Cu-Sm-Ce solid solution are weaker than those that are present in CeO_2 , so the metal-oxygen bonds tend to break and produce reactive oxygen species [74].

The oxygen peaks provide information about the oxidation states of cerium and confirm the coexistence of Ce^{4+} and Ce^{3+} . The O1s XPS spectra of calcined and sintered CSDCs are shown in Figures 10(c) and 10(d). Deconvolution of O1s core level spectra yields four peaks. The first peak (i) at ~ 528 eV is attributed to the lattice oxygen of $\text{Ce}^{4+}\text{-O}$ [73, 75]. The overlapping peak (ii) at ~ 529 eV is attributed to $\text{Ce}^{3+}\text{-O}$ [55, 58, 73] because $\text{Ce}^{3+}\text{-O}$ has a stronger bond than $\text{Ce}^{4+}\text{-O}$, so the binding energy of $\text{Ce}^{3+}\text{-O}$ is higher than that of $\text{Ce}^{4+}\text{-O}$ [55, 68, 73]. The third peak (iii) at ~ 531 eV corresponds to $\text{Sm}^{3+}\text{-O}$ because Sm has a higher electronegativity than Ce on the Pauling scale ($\text{Sm} = 1.71$ and $\text{Ce} = 1.12$) [55, 57], leading to higher binding energy. The last peak (iv) at ~ 533 eV is related to water adsorption [58] or oxygen species adsorption such as O^- , OH^- , and CO_3^{2-} [58, 75], resulting from reactions with $\text{V}_{\text{O}}^{\bullet\bullet}$ at the

nanoparticle surfaces [76] or nonstoichiometric oxygen [77]. The relative oxygen concentration of Ce^{3+} ($\text{O}_{1s}\text{Ce}^{3+}$) as present in Table 1 was calculated from the peak area of $\text{O}1s$ spectra as follows [58]:

$$\text{O}_{1s}\text{Ce}^{3+} = \frac{\text{O}_{1s}\text{Ce}^{3+}}{(\text{O}_{1s}\text{Ce}^{4+} + \text{O}_{1s}\text{Ce}^{3+} + \text{O}_{1s}\text{Sm}^{3+} + \text{O}_{1s}\text{ads.})}, \quad (14)$$

where $\text{O}_{1s}\text{Ce}^{4+}$, $\text{O}_{1s}\text{Sm}^{3+}$, and $\text{O}_{1s}\text{ads.}$ are oxygen concentrations of Ce^{4+} , Sm^{3+} , and oxygen adsorption, respectively.

The Ce^{3+} from XPS spectra may exist either in the Ce_2O_3 form or the $\text{Ce}^{3+}\text{-V}_\text{O}^{\bullet\bullet}$ form. The $\text{Ce}^{3+}\text{-V}_\text{O}^{\bullet\bullet}$ form created by the dopant cations substitution into Ce^{4+} ions can be verified by comparing the stoichiometry ratio (χ) with actual stoichiometry (χ'), which are calculated following equations (16) and (17), respectively [57]. If χ' is more than χ , the $\text{Ce}^{3+}\text{-V}_\text{O}^{\bullet\bullet}$ is formed without the presence of Ce_2O_3 ; however, if χ' is less than χ , Ce_2O_3 and $\text{Ce}^{3+}\text{-V}_\text{O}^{\bullet\bullet}$ co-exist [57, 78]. Table 1 lists the calculated value of χ and χ' for calcined and sintered CSDCs.

$$\chi = \frac{[\text{O}]}{[\text{Ce}]} = \frac{3}{2} [\text{Ce}^{3+}] + 2 [\text{Ce}^{4+}], \quad (15)$$

where $[\text{O}]$, $[\text{Ce}]$, $[\text{Ce}^{3+}]$, and $[\text{Ce}^{4+}]$ are the concentration of total oxygen, total Ce, Ce^{3+} , and Ce^{4+} , respectively.

$$\chi' = \frac{\text{O}_{1s}}{\text{Ce}^{3d}} = \frac{A_\text{O}}{A_\text{Ce}} \times \frac{S_\text{Ce}}{S_\text{O}}, \quad (16)$$

where O_{1s} denotes the total area under Ce peaks, Ce^{3d} denotes the total area under Ce peaks, and $S_\text{Ce}=7.399$ and $S_\text{O}=0.711$ denote sensitivity factors of Ce and O atoms, respectively.

For all sintered CSDCs, $\text{Ce}^{3+}\text{-V}_\text{O}^{\bullet\bullet}$ (related to $\text{CeO}_{2-\delta}$) is predominant in the sintered CSDC/DI and CSDC/CA since χ' is more than χ . Considering $[\text{Ce}^{3+}]$ values, the sintered CSDC/DI decreases from that of the calcined one because of the removal of hydroxide species, so Ce^{3+} turned into Ce^{4+} , and Ce^{4+} could subsequently partially reduce to Ce^{3+} at high temperature; thus, $\text{Ce}^{3+}\text{-V}_\text{O}^{\bullet\bullet}$ is predominant in the sintered CSDC/DI. In contrast, the $[\text{Ce}^{3+}]$ of sintered CSDC/CA is higher than that of the calcined one because the Cu ions diffuse from solid solution and could have reacted with Ce^{4+} ($\text{Cu}^+ + \text{Ce}^{4+} \rightarrow \text{Cu}^{2+} + \text{Ce}^{3+}$). Moreover, this effect takes place along with the thermally induced partial reduction of Ce^{4+} to Ce^{3+} , resulting in the domination of $\text{Ce}^{3+}\text{-V}_\text{O}^{\bullet\bullet}$. Although Ce_2O_3 and $\text{Ce}^{3+}\text{-V}_\text{O}^{\bullet\bullet}$ coexist in sintered CSDC/TA because χ' is less than χ , $\text{Ce}^{3+}\text{-V}_\text{O}^{\bullet\bullet}$ could still be a major species rather than Ce_2O_3 due to the decrease of $\text{Ce}^{3+}\text{-O}$ after sintering.

The high-resolution Sm 3d spectra of calcined and sintered CSDCs as shown in Figures S5(a) and S5(b) show the same characteristic, which consists of Sm $3d_{5/2}$ (~ 1082 eV) and Sm $3d_{3/2}$ (~ 1109 eV). The major peaks at ~ 1082 eV and ~ 1109 eV result from ionization of Sm^{3+} . The shoulder at ~ 1080 eV and ~ 1102 eV results from the strong charge transfer of unpaired electrons in 4f of Sm^{3+} [54], or Sm^{3+} segregation [79], or the result of electrostatic

interactions between a core level and a partially filled 4f level [80]. In our work, the shoulders of calcined and sintered CSDCs are possibly metastable SmO_8 -type complex or Sm_2O_3 nanodomains.

The C1s core level spectra at $\sim 288\text{--}290$ eV as shown in Figures S5(c) and S5(d) represent the presence of carbonate at the surface [58] and the C1s peaks at $\sim 284\text{--}286$ eV are ascribed to carbon [80]. All calcined and sintered CSDCs consist of carbonate species at ~ 290 eV, which is due to the adsorption of CO_x in ambient air or CO_x gases from complexing agents during combustion, in addition to cerium oxide since Cu dope CeO_2 also has been used in CO catalyst applications [69, 81, 82]. Furthermore, all of them have the C1s peaks at ~ 286 eV, which are assigned to carbon and are related to carbon trapped from complexing agents on nanoparticle surfaces.

The signal of Cu2p core level is fuzzy for both calcined and sintered CSDC powders, as shown in Figure 11(a) and 11(b). Curran et al. [83] reported that Cu = 0.01 could not be observed due to the detection limit of XPS. However, Cu species can only be detected in calcined CSDCs but not in sintered CSDCs due to Cu release at sintering temperature as well as Cu evaporation induced by the XPS laser. The Cu2p core level spectra of all calcined CSDCs are shown in Figure 11(c). The fitted peaks of $\text{Cu}2p_{3/2}$ and $\text{Cu}2p_{1/2}$ are at around ~ 933 eV and ~ 955 eV, respectively. Moreover, the Cu (II) satellite peaks at ~ 940 to ~ 945 eV are revealed. The $\text{Cu}2p_{3/2}$ peak at ~ 933 eV is ascribed to Cu^{2+} while the one at ~ 930 eV is characteristic of Cu^+ and/or Cu^0 [84]. Note that the presence of Cu^{2+} is also confirmed by the Raman result. However, the presence of Cu^+ and/or Cu^0 may arise from the reduction of Cu^{2+} , similar to the transformation of Ce^{4+} to Ce^{3+} under the testing conditions.

3.8. Pellet Characterization

3.8.1. SEM Images. The cross-sectional morphology of pellet samples after sintering was characterized using SEM as shown in Figure 12. After sintering, the pores in the figure are (1) pores from intergranular cracking and (2) pores in the bulk which are the combination of (i) interparticle voids and (ii) voids left behind by the evaporation of the volatile phase (copper segregation) [85]. Pore reduction requires the good redistribution of liquid copper segregation along grain boundaries, which starts at $\sim 750^\circ\text{C}$ for 1%mol Cu-20SDC [26]. The movement and merging of liquid Cu^{2+} promote particle mobility and particle rearrangement [25], which results in grain coarsening, especially when the particles are in contact, allowing the atoms at the surface of particles to diffuse and bridge, resulting in densification. However, the merging of the liquid phase in the voids of interparticle can also generate large pores when the liquid phase evaporates during sintering at 1100°C . Therefore, copper segregation could either increase or decrease densification for a certain sintering temperature. Despite having the highest amount of copper segregation in calcined CSDC/DI (based on Raman results), the CSDC/DI pellet is the least dense sample after sintering (Figure S5(b)). In the case of CSDC/DI, it may be

FIGURE 11: High-resolution Cu 2p XPS spectra of (a) calcined CSDCs raw data, (b) sintered CSDCs raw data, and (c) fitted calcined CSDCs.

FIGURE 12: Continued.

FIGURE 12: SEM cross-sectional images of (a) CSDC/DI, (b) CSDC/TA, and (c) CSDC/CA pellets.

because the portion of copper segregation in calcined CSDC/DI could evaporate earlier than copper in calcined CSDC/TA and CSDC/CA due to less Cu-Sm-Ce solid solution formation, resulting in CSDC/DI particles that cannot be properly rearranged. Furthermore, the amount of hydroxide phase, e.g., cerium hydroxide (based on Ce^{3+} in XPS results) in calcined CSDC/DI is higher than the others, which may prevent grain growth during sintering, leading to porosity development. The CSDC/CA pellet is the densest, yet it has the least amount of copper segregation in the calcined sample but the highest one in the sintered sample, which could be related to the diffusion of copper from solid solution when the temperature is raised above the calcination temperature. As a result, there is a large difference in the amount of copper segregation present in the calcined CSDC/CA as compared to that present in the sintered one (Figure S5(b)). From the Archimedes test, the relative densities (r.d.) of CSDC pellets are calculated from equation (1), which are $82.8 \pm 2.4\%$, $95.5 \pm 1.8\%$, and $97.8 \pm 0.9\%$ for CSDC/DI, CSDC/TA, and CSDC/CA, respectively.

Both r.d. and grain size can contribute to the change in grain and grain boundary conductivities, which was reported by Pérez-Coll et al. [5]. They reported that grain conductivity mainly depends on the r.d., while grain boundary conductivity was influenced by both r.d. and grain size. Generally, both conductivities of grain and grain boundary increase rapidly with increasing r.d. when the r.d. is lower than 91.9%. However, grain and grain boundary conductivities slightly arise when the r.d. is above 91.9% and above 93.9%, respectively. In addition, both grain and grain boundary conductivity slightly increases for grain sizes above $1.27 \mu\text{m}$ (93.9% r.d.). Therefore, grain and grain boundary conductivities of the sample are impacted by other factors when the r.d. exceeds 93.9%. Herein, the CSDC/TA and CSDC/CA samples are higher than 94% r.d., so the relationship of CSDCs conductivity with segregation and $V_{\text{O}}^{\bullet\bullet}$ is being investigated.

3.8.2. Grain Conductivity. Figure 13(a) shows an Arrhenius plot of $\ln(\sigma T)$ vs. $1000/T$ for grain conductivity. The grain conductivity of CSDC/CA is slightly higher than that of CSDC/TA and CSDC/DI at 350, 400, and 500°C because it

has a greater relative oxygen vacancy concentration than the others. However, the grain conductivity of CSDC/CA drops slightly lower than that of CSDC/TA at a temperature lower than 350°C because the $V_{\text{O}}^{\bullet\bullet}$ could be trapped by cation doped defects (Sm_{Ce}' , Ce_{Ce}' , Cu_{Ce}'' , and Cu_{Ce}''') and be blocked by the metastable SmO_8 complex and Sm_2O_3 nanodomains in the grain. As previously shown in Raman results, the relative amount of metastable SmO_8 complex is the highest in CSDC/CA after sintering, whereas the CSDC/DI has the lowest grain conductivity because it does not only have the lowest oxygen concentration and the lowest r.d. but also has high Sm_2O_3 nanodomains (Figure S4(a)).

3.8.3. Total Grain Boundary Conductivity. Copper segregation helps increase r.d., but it can also reduce grain boundary conductivities of samples. However, copper segregation could increase the total grain boundary conductivity due to the scavenging of SiO_2 contamination at grain boundary regions by copper [11]. The total grain boundary conductivities of all CSDCs (Figure 13(b)) are not significantly different above 300°C. At 250°C and 300°C, CSDC/DI has lower total grain boundary conductivity than CSDC/TA and CSDC/CA because CSDC/DI has the lowest r.d. and high content of Sm_2O_3 nanodomains despite having the lowest CuO segregation.

3.8.4. Specific Grain Boundary Conductivity. Specific grain boundary conductivity ($\sigma_{\text{gb}}^{\text{sp}}$) is commonly utilized to characterize the grain boundary conductivity behavior of polycrystalline materials based on the brick-layer model. The $C_{\text{g}}/C_{\text{gb}}$ normalization yields a specific grain boundary conductivity that is less dependent on grain size [32]. It can be calculated as follows [14, 86]:

$$\sigma_{\text{gb}}^{\text{sp}} = \frac{L}{AR_{\text{gb}}} \cdot \frac{C_{\text{g}}}{C_{\text{gb}}} = \sigma_{\text{gb}}^{\text{total}} \cdot \frac{C_{\text{g}}}{C_{\text{gb}}}, \quad (17)$$

where L is sample thickness, A is an active area, R_{gb} is grain boundary resistance, C_{g} is grain capacitance, C_{gb} is grain boundary capacitance, and $\sigma_{\text{gb}}^{\text{total}}$ is total grain boundary conductivity.

FIGURE 13: Arrhenius plot of (a) grain conductivity, (b) total grain boundary conductivity, (c) specific grain boundary, and (d) total conductivity.

The σ_{gb}^{sp} of GDC without sintering aids is slightly affected by grain size and r.d. if the r.d. is greater than 75% because it is only affected by geometrical effect [5]. The geometrical effects are explained by the formula: $C_{gb} = \epsilon_0 \epsilon_{gb} (A/L_{gb})$ [86], where C_{gb} increases with a shorter effective pathway and larger effective cross section area per grain and with decreasing σ_{gb}^{sp} . Since the C_{gb} is attributed to SiO₂ contamination, CuO and Sm₂O₃ segregation, and depletion regions, the σ_{gb}^{sp} decreases as segregations and depletion regions increase. The σ_{gb}^{sp} , as presented in Figure 13(c), are estimated at temperatures below 400°C due to the existing C_g and C_{gb} . Herein, the grain boundary capacitances are in the range of 9–30 nF as shown in Table 2. The C_{gb} values are arranged in the following order: CSDC/DI < CSDC/TA < CSDC/CA. The high C_{gb} of CSDC/CA could be an indication of

segregations or a wider depletion region in the samples. Considering the segregations from Raman results after sintering (Figure S4), the segregation of CuO is in the following order: CSDC/DI < CSDC/TA < CSDC/CA, whereas Sm₂O₃ nanodomains are as follows: CSDC/DI $\approx$ CSDC/TA > CSDC/CA. Herein, the σ_{gb}^{sp} of CSDC/DI is slightly lower than that of CSDC/TA because the amount of CuO segregation in CSDC/TA is higher than that in CSDC/DI. Despite having more CuO segregation than CSDC/DI, CSDC/TA has a slightly higher σ_{gb}^{sp} due to better densification than CSDC/DI. The CSDC/CA has the lowest σ_{gb}^{sp} because it has the highest amount of CuO segregated. The highest amount of CuO segregation for sintered CSDC/CA should be related to Cu diffusion from Cu-Sm-Ce solid solution during sintering and subsequent precipitation along

TABLE 2: The comparison of grain boundary capacitances of CSDCs at temperatures ranging from 250 to 350°C.

Temperature (°C)	Grain boundary capacitance (nF)		
	CSDC/DI	CSDC/TA	CSDC/CA
350	9.50	13.9	27.8
300	9.34	14.1	29.6
250	9.16	13.1	27.0

the grain boundaries. The black color on the surface of CSDC/CA pellet and in the bulk can be a CuO precipitate. According to Raman results (Figure 4S), sintered CSDC/DI and CSDC/TA have more Sm_2O_3 nanodomains than sintered CSDC/CA. However, the amount of CuO is higher than that of Sm_2O_3 nanodomains, around tenfold. As the result, it is possible to conclude that CuO segregation mainly affects $\sigma_{\text{gb}}^{\text{sp}}$ rather than Sm_2O_3 nanodomains. Note that even though CSDC/CA has the highest $\sigma_{\text{gb}}^{\text{sp}}$, its total grain boundary conductivity is the same as CSDC/DI and CSDC/TA. The difference between the $\sigma_{\text{gb}}^{\text{tot}}$ and $\sigma_{\text{gb}}^{\text{sp}}$ may be that the true area of grain boundary is not used for calculating $\sigma_{\text{gb}}^{\text{tot}}$.

3.8.5. Total Conductivity. The total conductivities of CSDCs were measured at temperatures ranging from 250 to 800°C, as shown in Figure 13(d). The total conductivity is the summation of grain and grain boundary conductivities, which are affected by the concentration of $V_{\text{O}}^{\bullet\bullet}$, CuO segregation, r.d., and Sm_2O_3 nanodomains. In our work, grain conductivity mainly depends on $V_{\text{O}}^{\bullet\bullet}$, whereas grain boundary conductivity is influenced by CuO segregation and r.d. The activation energy (E_a) is correlated to the slope of the Arrhenius plot of total conductivity, as shown in Table 3. The E_a can be extracted from two regimes: the high-temperature range (500–800°C) and the low-temperature range (250–400°C). Moreover, the E_a is related to enthalpy of migration (ΔH_m) in the high-temperature range, whereas E_a corresponds to both ΔH_m and enthalpy of association (ΔH_a) in the low-temperature range. The ΔH_m involves the vacancies jumping to neighboring sites, while the ΔH_a corresponds to trapped vacancies or immobilized dopant ions at the low-temperature range [10]. The samples with high total conductivity may need a low E_a value. Despite having a higher CuO segregation than CSDC/DI, the CSDC/CA and CSDC/TA have higher total conductivities than CSDC/DI due to higher $V_{\text{O}}^{\bullet\bullet}$ and r.d. However, the segregation of CuO along grain boundaries slightly affects the total conductivity at temperatures above 400°C, which is caused by the increasing mobility of $V_{\text{O}}^{\bullet\bullet}$. At the high-temperatures range, the sum of effects contributed by the difference in $V_{\text{O}}^{\bullet\bullet}$, CuO segregation, and r.d. lead to the insignificant difference in the ΔH_m . Furthermore, the ΔH_a of CSDC/DI, CSDC/TA, and CSDC/CA are 0.16, 0.19, and 0.23 eV, respectively. The difference in ΔH_a values is caused by the various amounts of segregated CuO along the grain boundaries, as well as the defect association between $V_{\text{O}}^{\bullet\bullet}$ and the cation dopant [4]. However, the total conductivity of CSDC/CA is the highest because it has the highest grain conductivity. The total conductivities of CSDC/DI, CSDC/TA, and CSDC/CA are

TABLE 3: The relative density, the activation energy ($E_{a,\text{LT}}$) at low temperatures (250–400°C), the enthalpy of migration (ΔH_m), and the enthalpy of association (ΔH_a).

Sample	Relative density (%)	ΔH_m (eV)	$E_{a,\text{LT}}$ (eV)	ΔH_a (eV) ^a
CSDC/DI	82.78	0.73	0.88	0.16
CSDC/TA	95.51	0.72	0.91	0.19
CSDC/CA	97.78	0.71	0.94	0.23

$$^a \Delta H_a = E_{a,\text{LT}} - \Delta H_m.$$

TABLE 4: The comparison of total conductivity at 600°C to those reported in previously published works.

%Sm	%Cu	Conductivity (S/cm)	References
20	1	0.0146	Lü et al. [31]
20	1	0.0154	Dong et al. [15]
20	1	0.0060	Toor and Croiset [25]
20	3	0.0088	Toor and Croiset [87]
20	5	0.0110	Toor and Croiset [87]
20	1	0.0173	Zhang et al. [26]
19	1	0.0176	Our work on CSDC/DI
19	1	0.0228	Our work on CSDC/TA
19	1	0.0271	Our work on CSDC/CA

0.0176, 0.0228, and 0.0271 S/cm² at 600°C, respectively. Table 4 shows a comparison of total conductivities at 600°C between this work and other works.

4. Conclusions

The CSDC samples were successfully synthesized via a sol-gel auto-combustion method with and without complexing agents. CA or TA was a complexing agent used for this study, which also served as fuel. The as-synthesized morphology of CSDC/DI shows both layered structure and small agglomerate particles, while those of CSDC/TA and CSDC/CA reveal dense-xerogel and porous xerogel, respectively. The porous structure observed in as-synthesized CSDC/CA is the result of bubble generation and expansion during the gas-release stage, since the CA has a higher degree of cross-linking. Moreover, calcined CSDC/CA has higher extrinsic oxygen vacancies than calcined CSDC/TA, indicating greater solubility of Sm^{3+} and Cu^{2+} in ceria because CA can complex with metal ions better than TA. Such improved complexing results in well-dispersed metal ions. The total oxygen vacancies in sintered CSDCs are lower than those of calcined CSDCs due to the partial oxidation of Ce^{3+} to Ce^{4+} . The trend of relative total oxygen vacancy concentrations of sintered CSDCs is as follows: CSDC/CA > CSDC/TA > CSDC/DI. The calcined CSDCs also follow the same pattern. From Raman analysis, the presence of copper segregation, Sm_2O_3 nanodomains, and metastable SmO_8 complex are observed in calcined and sintered CSDCs. The segregation of Cu^{2+} is the key factor rather than that of Sm_2O_3 nanodomains and metastable SmO_8 complex in determining the grain boundary behavior because the

relative concentration of Cu^{2+} is tenfold higher than those of other factors. Although calcined CSDC/DI has the highest amount of copper segregation, it has poor densification as some liquid copper especially in the interparticle space could evaporate before the CSDC/DI particles could properly rearrange. On the contrary, calcined CSDC/CA has the lowest amount of copper segregation yet it has the highest densification, which could be due to the diffusion of Cu ions from Cu-Sm-Ce solid solution during the particle arrangement stage. The relative densities of CSDC/DI, CSDC/TA, and CSDC/CA are $82.8 \pm 2.4\%$, $95.5 \pm 1.8\%$, and $97.8 \pm 0.9\%$, respectively. The highest CuO segregates are also observed in sintered CSDC/CA, implying the diffusion of Cu from Cu-Sm-Ce solid solution during the sintering process. Specific grain boundary conductivity, which is governed by the segregation of CuO along grain boundaries, can well describe the true behavior of grain boundary conductivity. The highest value of ΔH_a of CSDC/CA at the low-temperature range, which coincides with their lowest specific grain boundary conductivity, indicates that grain boundaries are covered by CuO. It is worth noting that the CuO segregation has little effect on the total grain boundary conductivity of CSDC/CA at temperatures above 400°C . The overall conductivity of CSDC/TA is slightly lower than that of CSDC/CA. The total conductivities at 600°C are 0.0176, 0.0228, and 0.0271 S/cm for CSDC/DI, CSDC/TA, and CSDC/CA, respectively.

Data Availability

The raw data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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Supplementary Materials

The XRD peaks shift of calcined SDC and calcined CSDC powders, the relative concentration of CuO and Sm_2O_3 segregation of calcined and sintered CSDCs from Raman analysis, and the high-resolution XPS spectra of Sm3d and C1s for calcined and sintered CSDCs. (*Supplementary Materials*)

References

- [1] A. Zarkov, A. Stanulis, T. Salkus et al., "Synthesis of nano-crystalline gadolinium doped ceria via sol-gel combustion and sol-gel synthesis routes," *Ceramics International*, vol. 42, no. 3, pp. 3972–3988, 2016.
- [2] Z. Fu, Q. Sun, D. Ma, N. Zhang, Y. An, and Z. Yang, "Effects of Sm doping content on the ionic conduction of CeO_2 in SOFCs from first principles," *Applied Physics Letters*, vol. 111, no. 2, Article ID 023903, 2017.
- [3] N. Cioateră, V. Părvulescu, A. Rolle, and R. N. Vannier, "Enhanced ionic conductivity of Sm, Gd-doped ceria induced by modification of powder synthesis procedure," *Ceramics International*, vol. 38, pp. 5461–5468, 2012.
- [4] K. C. Anjaneya, G. P. Nayaka, J. Manjanna, G. Govindaraj, and K. N. Ganesha, "Preparation and characterization of $\text{Ce}_{1-x}\text{Sm}_x\text{O}_{2-\delta}$ ($x = 0.1-0.3$) as electrolyte material for intermediate temperature SOFC," *Solid State Sciences*, vol. 26, pp. 89–96, 2013.
- [5] D. Pérez-Coll, E. Sánchez-López, and G. C. Mather, "Influence of porosity on the bulk and grain-boundary electrical properties of Gd-doped ceria," *Solid State Ionics*, vol. 181, no. 21–22, pp. 1033–1042, 2010.
- [6] S. Anirban, T. Paul, and A. Dutta, "Vacancy mediated ionic conduction in Dy substituted nanoceria: a structure-property correlation study," *RSC Advances*, vol. 5, no. 62, pp. 50186–50195, 2015.
- [7] G. Accardo, G. Dell'Agli, L. Spiridigliozzi, S. P. Yoon, and D. Frattini, "On the oxygen vacancies optimization through Pr co-doping of ceria-based electrolytes for electrolyte-supported solid oxide fuel cells," *International Journal of Hydrogen Energy*, vol. 45, no. 38, pp. 19707–19719, 2020.
- [8] K. C. Anjaneya, G. P. Nayaka, J. Manjanna, G. Govindaraj, and K. N. Ganesha, "Studies on structural, morphological and electrical properties of $\text{Ce}_{0.8}\text{Ln}_{0.2}\text{O}_{2-\delta}$ ($\text{Ln} = \text{Y}^{3+}$, Gd^{3+} , Sm^{3+} , Nd^{3+} and La^{3+}) solid solutions prepared by citrate complexation method," *Journal of Alloys and Compounds*, vol. 585, pp. 594–601, 2014.
- [9] S. Anirban and A. Dutta, "Structural and ionic transport mechanism of rare earth doped cerium oxide nanomaterials: effect of ionic radius of dopant cations," *Solid State Ionics*, vol. 309, pp. 137–145, 2017.
- [10] J. Koettgen, S. Grieshammer, P. Hein, B. O. H. Grope, M. Nakayama, and M. Martin, "Understanding the ionic conductivity maximum in doped ceria: trapping and blocking," *Physical Chemistry Chemical Physics*, vol. 20, no. 21, pp. 14291–14321, 2018.
- [11] P. Arunkumar, M. Meena, and K. S. Babu, "A review on cerium oxide-based electrolytes for ITSOFC," *Nanomaterials and Energy*, vol. 1, no. 5, pp. 288–305, 2012.
- [12] G. Kim, N. Lee, K.-B. Kim et al., "Various synthesis methods of aliovalent-doped ceria and their electrical properties for intermediate temperature solid oxide electrolytes," *International Journal of Hydrogen Energy*, vol. 38, no. 3, pp. 1571–1587, 2013.
- [13] A. Arabaci and Ö. Serin, "Characterization of Sm-doped ceria ceramics synthesized by two different methods," *Journal of Materials Engineering and Performance*, vol. 24, no. 7, pp. 2730–2737, 2015.
- [14] Z. Khakpour, A. Yuzbashi, A. Maghsodipour, and K. Ahmadi, "Electrical conductivity of Sm-doped CeO_2 electrolyte produced by two-step sintering," *Solid State Ionics*, vol. 227, pp. 80–85, 2012.
- [15] Y. Dong, S. Hampshire, J.-E. Zhou, X. Dong, B. Lin, and G. Meng, "Combustion synthesis and characterization of Cu-

- Sm co-doped CeO_2 electrolytes,” *Journal of the European Ceramic Society*, vol. 31, no. 13, pp. 2365–2376, 2011.
- [16] Y. Dong, S. Hampshire, B. Lin, Y. Ling, and X. Zhang, “High sintering activity Cu-Gd co-doped CeO_2 electrolyte for solid oxide fuel cells,” *Journal of Power Sources*, vol. 195, no. 19, pp. 6510–6515, 2010.
 - [17] Y. Dong, S. Hampshire, J. E. Zhou, and G. Meng, “Synthesis and sintering of Gd-doped CeO_2 electrolytes with and without 1 at.% CuO doping for solid oxide fuel cell applications,” *International Journal of Hydrogen Energy*, vol. 36, pp. 5054–5066, 2011.
 - [18] G. Accardo, C. Ferone, R. Cioffi, D. Frattini, L. Spiridigliozzi, and G. Dell’Aglì, “Electrical and microstructural characterization of ceramic gadolinium-doped ceria electrolytes for ITSOFCs by sol-gel route,” *Journal of Applied Biomaterials & Functional Materials*, vol. 14, no. 1, pp. 35–41, 2016.
 - [19] Y. Han, S. Li, X. Wang, and X. Chen, “Synthesis and sintering of nanocrystalline hydroxyapatite powders by citric acid sol-gel combustion method,” *Materials Research Bulletin*, vol. 39, no. 1, pp. 25–32, 2004.
 - [20] T. H. Santos, J. P. F. Grilo, F. J. A. Loureiro, D. P. Fagg, F. C. Fonseca, and D. A. Macedo, “Structure, densification and electrical properties of Gd^{3+} and Cu^{2+} co-doped ceria solid electrolytes for SOFC applications: effects of Gd_2O_3 content,” *Ceramics International*, vol. 44, no. 3, pp. 2745–2751, 2018.
 - [21] C. G. M. Lima, T. H. Santos, J. P. F. Grilo et al., “Synthesis and properties of CuO-doped $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$ electrolytes for SOFCs,” *Ceramics International*, vol. 41, no. 3, pp. 4161–4168, 2015.
 - [22] T. Mahata, G. Das, R. K. Mishra, and B. P. Sharma, “Combustion synthesis of gadolinia doped ceria powder,” *Journal of Alloys and Compounds*, vol. 391, no. 1–2, pp. 129–135, 2005.
 - [23] M. Singh and A. K. Singh, “Studies on structural, morphological, and electrical properties of Ga^{3+} and Cu^{2+} co-doped ceria ceramics as solid electrolyte for IT-SOFCs,” *International Journal of Hydrogen Energy*, vol. 45, no. 44, pp. 24014–24025, 2019.
 - [24] S. Anirban, P. T. Das, and A. Dutta, “Effect of divalent cation addition on structure, conductivity and grain boundary properties in La doped ceria oxygen ion conductors,” *Ceramics International*, vol. 45, no. 5, pp. 5751–5760, 2019.
 - [25] S. Y. Toor and E. Croiset, “Reducing sintering temperature while maintaining high conductivity for SOFC electrolyte: copper as sintering aid for samarium doped ceria,” *Ceramics International*, vol. 46, no. 1, pp. 1148–1157, 2020.
 - [26] X. Zhang, C. Decès-Petit, S. Yick et al., “A study on sintering aids for $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ electrolyte,” *Journal of Power Sources*, vol. 162, no. 1, pp. 480–485, 2006.
 - [27] T. Zhu, Y. Lin, Z. Yang et al., “Evaluation of Li_2O as an efficient sintering aid for gadolinia-doped ceria electrolyte for solid oxide fuel cells,” *Journal of Power Sources*, vol. 261, pp. 255–263, 2014.
 - [28] S. Anirban and A. Dutta, “An insight into the structure, conductivity and ion dynamics of Sr-Sm co-doped ceria oxygen ion conductors: effect of defect interaction,” *Solid State Sciences*, vol. 86, pp. 69–76, 2018.
 - [29] L. A. Villas-Boas, F. M. L. Figueiredo, D. P. F. de Souza, and F. M. B. Marques, “Zn as sintering aid for ceria-based electrolytes,” *Solid State Ionics*, vol. 262, pp. 522–525, 2014.
 - [30] A. V. Nikonov, A. V. Spirin, V. R. Khrustov et al., “Synthesis and properties of solid electrolyte $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$ with Co, Cu, Mn, Zn doping,” *Inorganic Materials*, vol. 52, no. 7, pp. 708–715, 2016.
 - [31] Q. Lü, X. Dong, Z. Zhu, and Y. Dong, “Effect of CuO doping on sinterability, mechanical and electrical properties of Sm-doped CeO_2 ceramic thick membrane solid electrolytes,” *Ceramics International*, vol. 40, no. 10, pp. 15545–15550, 2014.
 - [32] E. C. C. Souza, W. C. Chueh, W. Jung, E. N. S. Muccillo, and S. M. Haile, “Ionic and electronic conductivity of nanostructured, Samaria-doped ceria,” *Journal of the Electrochemical Society*, vol. 159, no. 5, pp. K127–K135, 2012.
 - [33] E. A. Cochran, K. N. Woods, D. W. Johnson, C. J. Page, and S. W. Boettcher, “Unique chemistries of metal-nitrate precursors to form metal-oxide thin films from solution: materials for electronic and energy applications,” *Journal of Materials Chemistry*, vol. 7, no. 42, pp. 24124–24149, 2019.
 - [34] A. Malecki, R. Gajerski, S. Łabuś, B. Prochowska-Klisch, and K. T. Wojciechowski, “Mechanism of thermal decomposition of d-metals nitrates hydrates,” *Journal of Thermal Analysis and Calorimetry*, vol. 60, pp. 17–23, 2000.
 - [35] B. Ambrozini, P. R. Dametto, A. B. Siqueira, C. T. Carvalho, and M. Ionashiro, “Synthesis, characterization and thermal behavior on solid tartrates of light trivalent lanthanides,” *Journal of Thermal Analysis and Calorimetry*, vol. 97, no. 2, pp. 761–764, 2009.
 - [36] Z. Ding, R. L. Frost, and J. T. Klopogge, “Thermal activation of copper carbonate,” *Journal of Materials Science Letters*, vol. 21, no. 13, pp. 981–983, 2002.
 - [37] H. V. Fajardo, E. Longo, E. R. Leite, R. Libanori, L. F. D. Probst, and N. L. V. Carreño, “Synthesis, characterization and catalytic properties of nanocrystalline Y_2O_3 -coated TiO_2 in the ethanol dehydration reaction,” *Materials Research*, vol. 15, no. 2, pp. 285–290, 2012.
 - [38] C. D. Wu, C. Z. Lu, S. F. Lu, H. H. Zhuang, and J. S. Huang, “Synthesis, structures and properties of a series of novel left- and right-handed metal coordination double helicates with chiral channels,” *Dalton Transactions*, vol. 16, pp. 3192–3198, 2003.
 - [39] K. Guo, H. H. Chen, X. Guo, X. X. Yang, F. F. Xu, and J. T. Zhao, “Morphology investigation of yttrium aluminum garnet nano-powders prepared by a sol-gel combustion method,” *Journal of Alloys and Compounds*, vol. 500, no. 1, pp. 34–38, 2010.
 - [40] J. Calvache-Muñoz, F. A. Prado, and J. E. Rodríguez-Páez, “Cerium oxide nanoparticles: synthesis, characterization and tentative mechanism of particle formation,” *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 529, pp. 146–159, 2017.
 - [41] T. Mokkalbost, I. Kaus, T. Grande, and M. A. Einarsrud, “Combustion synthesis and characterization of nanocrystalline CeO_2 -based powders,” *Chemistry of Materials*, vol. 16, no. 25, pp. 5489–5494, 2004.
 - [42] L. Chen, P. Fleming, V. Morris, J. D. Holmes, and M. A. Morris, “Size-related lattice parameter changes and surface defects in ceria nanocrystals,” *Journal of Physical Chemistry C*, vol. 114, no. 30, pp. 12909–12919, 2010.
 - [43] N. Maheswari and G. Muralidharan, “Hexagonal CeO_2 nanostructures: an efficient electrode material for supercapacitors,” *Dalton Transactions*, vol. 45, no. 36, pp. 14352–14362, 2016.
 - [44] G. JayaKumar, A. Albert Irudayaraj, and A. Dhayal Raj, “Investigation on the synthesis and photocatalytic activity of activated carbon–cerium oxide (AC-CeO_2) nanocomposite,” *Applied Physics A*, vol. 125, 2019.
 - [45] F. Kalyk, A. Stankevičiūtė, G. Budrytė et al., “Comparative study of samarium-doped ceria nanopowders synthesized by

- various chemical synthesis routes," *Ceramics International*, vol. 46, no. 15, 2020.
- [46] J. Ning, Y. Zhou, A. Chen, Y. Li, S. Miao, and W. Shen, "Dispersion of copper on ceria for the low-temperature water-gas shift reaction," *Catalysis Today*, vol. 357, 2019.
 - [47] A. A. AlKhoori, K. Polychronopoulou, A. Belabbes et al., "Cu, Sm Co-Doping effect on the CO oxidation activity of CeO₂. A combined experimental and density functional study," *Applied Surface Science*, vol. 521, Article ID 146305, 2020.
 - [48] E. Sartoretti, C. Novara, F. Giorgis et al., "In situ Raman analyses of the soot oxidation reaction over nanostructured ceria-based catalysts," *Scientific Reports*, vol. 9, no. 1, p. 3875, 2019.
 - [49] M. Guo, J. Lu, Y. Wu, Y. Wang, and M. Luo, "UV and visible Raman studies of oxygen vacancies in rare-earth-doped ceria," *Langmuir*, vol. 27, no. 7, pp. 3872–3877, 2011.
 - [50] C. Artini, M. M. Carnasciali, J. R. Plaisier, G. A. Costa, and M. Pani, "A novel method for the evaluation of the rare earth (RE) coordination number in RE-doped ceria through Raman spectroscopy," *Solid State Ionics*, vol. 311, pp. 90–97, 2017.
 - [51] C. Artini, M. Pani, M. M. Carnasciali, J. R. Plaisier, and G. A. Costa, "Lu-, Sm-, and Gd-doped ceria: a comparative approach to their structural properties," *Inorganic Chemistry*, vol. 55, no. 20, pp. 10567–10579, 2016.
 - [52] A. Zarkov, L. Mikoliunaite, A. Katelnikovas, S. Tautkus, and A. Kareiva, "Preparation by different methods and analytical characterization of gadolinium-doped ceria," *Chemical Papers*, vol. 72, no. 1, pp. 129–138, 2018.
 - [53] E. Sartoretti, C. Novara, M. Fontana et al., "New insights on the defect sites evolution during CO oxidation over doped ceria nanocatalysts probed by in situ Raman spectroscopy," *Applied Catalysis A: General*, vol. 596, Article ID 117517, 2020.
 - [54] R. Tao, J. Xu, H. Zhong et al., "Finely tuned structure and catalytic performance of cerium oxides by a continuous samarium doping from 0 to 100%," *Inorganic Chemistry*, vol. 58, pp. 13066–13076, 2019.
 - [55] S. A. Acharya, V. M. Gaikwad, S. W. D'Souza, and S. R. Barman, "Gd/Sm dopant-modified oxidation state and defect generation in nano-ceria," *Solid State Ionics*, vol. 260, pp. 21–29, 2014.
 - [56] C. Artini, M. Pani, M. M. Carnasciali, M. T. Buscaglia, J. R. Plaisier, and G. A. Costa, "Structural features of Sm- and Gd-doped ceria studied by synchrotron X-ray diffraction and μ -Raman spectroscopy," *Inorganic Chemistry*, vol. 54, no. 8, pp. 4126–4137, 2015.
 - [57] S. Soni, N. Chouhan, R. K. Meena et al., "Electronic structure and room temperature ferromagnetism in Gd-doped cerium oxide nanoparticles for hydrogen generation via photocatalytic water splitting," *Global Challenges*, vol. 3, no. 5, Article ID 1800090, 2019.
 - [58] D. Mukherjee, B. G. Rao, and B. M. Reddy, "Characterization of ceria-based nano-oxide catalysts by Raman spectroscopy," *Topics in Catalysis*, vol. 60, no. 19–20, pp. 1673–1681, 2017.
 - [59] M. Rashad, M. Rüsing, G. Berth, K. Lischka, and A. Pawlis, "CuO and Co₃O₄ nanoparticles: synthesis, characterizations, and Raman spectroscopy," *Journal of Nanomaterials*, vol. 2013, Article ID 714853, 6 pages, 2013.
 - [60] A. Filtschew, K. Hofmann, and C. Hess, "Ceria and its defect structure: new insights from a combined spectroscopic approach," *Journal of Physical Chemistry C*, vol. 120, no. 12, pp. 6694–6703, 2016.
 - [61] S. Aškračić, Z. Dohčević-Mitrović, A. Kremenović, N. Lazarević, V. Kahlenberg, and Z. V. Popović, "Oxygen vacancy-induced microstructural changes of annealed CeO₂-x nanocrystals," *Journal of Raman Spectroscopy*, vol. 43, pp. 76–81, 2012.
 - [62] R. Schmitt, A. Nanning, O. Kraynis et al., "A review of defect structure and chemistry in ceria and its solid solutions," *Chemical Society Reviews*, vol. 49, no. 2, pp. 554–592, 2020.
 - [63] K. Chen and D. Xue, "Reaction route to the crystallization of copper oxides," *Applied Science and Convergence Technology*, vol. 23, no. 1, 2014.
 - [64] S. A. Acharya, V. M. Gaikwad, V. Sathe, and S. K. Kulkarni, "Influence of gadolinium doping on the structure and defects of ceria under fuel cell operating temperature," *Applied Physics Letters*, vol. 104, no. 11, Article ID 113508, 2014.
 - [65] W. Shan, Z. Feng, Z. Li, J. Zhang, W. Shen, and C. Li, "Oxidative steam reforming of methanol on CeCuO catalysts prepared by deposition? Precipitation, coprecipitation, and complexation? combustion methods," *Journal of Catalysis*, vol. 228, no. 1, pp. 206–217, 2004.
 - [66] C. Artini, M. M. Carnasciali, M. Viviani et al., "Structural properties of Sm-doped ceria electrolytes at the fuel cell operating temperatures," *Solid State Ionics*, vol. 315, pp. 85–91, 2018.
 - [67] R. Kostić, S. Aškračić, Z. Dohčević-Mitrović, and Z. V. Popović, "Low-frequency Raman scattering from CeO₂ nanoparticles," *Applied Physics A*, vol. 90, pp. 679–683, 2008.
 - [68] S. Preethi, M. Abhiroop, and K. Suresh Babu, "Low temperature densification by lithium co-doping and its effect on ionic conductivity of samarium doped ceria electrolyte," *Ceramics International*, vol. 45, no. 5, pp. 5819–5828, 2019.
 - [69] K. Chang, H. Zhang, M. J. Cheng, and Q. Lu, "Application of ceria in CO₂ conversion catalysis," *ACS Catalysis*, vol. 10, no. 1, pp. 613–631, 2020.
 - [70] X. Wang, J. A. Rodriguez, J. C. Hanson, D. Gamarrá, A. Martínez-Arias, and M. Fernández-García, "In situ studies of the active sites for the water gas shift reaction over Cu–CeO₂ catalysts: complex interaction between metallic copper and oxygen vacancies of ceria," *The Journal of Physical Chemistry B*, vol. 110, no. 1, pp. 428–434, 2006.
 - [71] C. Aliotta, L. F. Liotta, V. La Parola et al., "Ceria-based electrolytes prepared by solution combustion synthesis: the role of fuel on the materials properties," *Applied Catalysis B: Environmental*, vol. 197, pp. 14–22, 2016.
 - [72] Y. Zhu, N. Jain, M. K. Hudait, D. Maurya, R. Varghese, and S. Priya, "X-ray photoelectron spectroscopy analysis and band offset determination of CeO₂ deposited on epitaxial (100), (110), and (111)Ge," *Journal of Vacuum Science & Technology B, Nanotechnology and Microelectronics: Materials, Processing, Measurement, and Phenomena*, vol. 32, no. 1, Article ID 011217, 2014.
 - [73] G. H. Jaffari, A. Imran, M. Bah et al., "Identification and quantification of oxygen vacancies in CeO₂ nanocrystals and their role in formation of F-centers," *Applied Surface Science*, vol. 396, pp. 547–553, 2017.
 - [74] H. Lan, G. Zhou, L. Cuijuan, Y. Yu, H. Xie, and G. Zhang, "High efficiency CeCu composite oxide catalysts improved via preparation methods for propyl acetate catalytic combustion in air," *International Journal of Chemical Reactor Engineering*, vol. 14, 2016.
 - [75] Y. Liu, L. Fan, Y. Cai, W. Zhang, B. Wang, and B. Zhu, "Superionic conductivity of Sm³⁺, Pr³⁺, and Nd³⁺ triple-doped ceria through bulk and surface two-step doping approach," *ACS Applied Materials & Interfaces*, vol. 9, no. 28, pp. 23614–23623, 2017.
 - [76] X. Garcia, L. Soler, N. J. Divins et al., "Ceria-based catalysts studied by near ambient pressure X-ray photoelectron spectroscopy: a review," *Catalysts*, vol. 10, no. 3, p. 286, 2020.

- [77] X. Wang, X. Wang, Q. Di, H. Zhao, B. Liang, and J. Yang, "Mutual effects of fluorine dopant and oxygen vacancies on structural and luminescence characteristics of F doped SnO_2 nanoparticles," *Materials*, vol. 10, no. 12, p. 1398, 2017.
- [78] S. Chahal, A. Kumar, and P. Kumar, "Erbium-doped oxygen deficient cerium oxide: bi-functional material in the field of spintronics and photocatalysis," *Applied Nanoscience*, vol. 10, no. 6, pp. 1721–1733, 2020.
- [79] N. Yang, P. Orgiani, E. Di Bartolomeo et al., "Effects of dopant ionic radius on cerium reduction in epitaxial cerium oxide thin films," *Journal of Physical Chemistry C*, vol. 121, no. 16, pp. 8841–8849, 2017.
- [80] P. Datta, P. Majewski, and F. Aldinger, "Study of gadolinia-doped ceria solid electrolyte surface by XPS," *Materials Characterization*, vol. 60, no. 2, pp. 138–143, 2009.
- [81] J. Song, P. P. Rodenbough, W. Xu, S. D. Senanayake, and S. W. Chan, "Reduction of nano- Cu_2O : crystallite size dependent and the effect of nano-ceria support," *Journal of Physical Chemistry C*, vol. 119, no. 31, pp. 17667–17672, 2015.
- [82] S. Dey and G. C. Dhal, "Cerium catalysts applications in carbon monoxide oxidations," *Materials Science for Energy Technologies*, vol. 3, pp. 6–24, 2020.
- [83] C. D. Curran, L. Lu, C. J. Kiely, and S. McIntosh, "Ambient temperature aqueous synthesis of ultrasmall copper doped ceria nanocrystals for the water gas shift and carbon monoxide oxidation reactions," *Journal of Materials Chemistry*, vol. 6, no. 1, pp. 244–255, 2018.
- [84] T. Kou, C. Si, J. Pinto, C. Ma, and Z. Zhang, "Dealloying assisted high-yield growth of surfactant-free highly active Cu-doped CeO_2 nanowires for low-temperature CO oxidation," *Nanoscale*, vol. 9, no. 23, pp. 8007–8014, 2017.
- [85] R. M. German, P. Suri, and S. J. Park, "Review: liquid phase sintering," *Journal of Materials Science*, vol. 44, no. 1, pp. 1–39, 2009.
- [86] J. Tao, A. Dong, and J. Wang, "The influence of microstructure and grain boundary on the electrical properties of scandia stabilized zirconia," *Materials Transactions*, vol. 54, no. 5, pp. 825–832, 2013.
- [87] S. Y. Toor and E. Croiset, "Effects of copper oxide addition on the electrochemical properties of samarium doped ceria electrolyte for intermediate temperature solid oxide fuel cells," *ECS Transactions*, vol. 68, no. 1, pp. 387–394, 2015.