Influences of Annealing Temperature and Doping Concentration on Microstructural and Optical Properties of $\text{CeO}_2\text{:Sm}^{3+}$ Nanocrystals

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Abstract Nanocrystals of CeO_2 with different doping concentrations of Sm^{3+} were synthesized by a novel and cost-effective method. The crystal structure, morphology and particle size were systematically investigated by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. Effects of the annealing temperature and doping concentrations on the microstructural properties of the crystals were studied. X-ray diffraction analysis indicates that the cubic structure of the CeO_2 is not affected by the doping of Sm^{3+} up to a doping concentration of 20%. Different structural parameters such as lattice constant, surface area, bulk density and porosity of the crystal were determined and discussed. Microscopic images of the $\text{CeO}_2\text{:Sm}^{3+}$ suggest that the thermal decomposition of oxalate precursor is a suitable synthesis pathway to produce uniform-sized microparticles and nanoparticles. The influences of annealing temperature and doping concentration of Sm^{3+} on the optical properties of the nanocrystals were also discussed. The photoluminescence excitation spectra reveal that the charge transfer band is redshifted with increasing annealing temperatures. Emission attains its maximum intensity for Sm^{3+} concentration of 1%, and higher concentrations lead to emission quenching.

KEY WORDS: Microstructure; Strain; Photoluminescence; $\text{CeO}_2\text{:Sm}^{3+}$ nanocrystal; Doping concentration; Annealing temperature

1 Introduction

Nanostructured materials have received a tremendous amount of attention during the past few decades owing to their versatile applications in most fields of modern technology. The novel and intriguing physical properties when compared to their bulk counterparts are attributed to the large surface to volume ratio, quantum confinement, and changes in the lattice parameter and symmetry. Rare earth oxide nanostructured materials have played a major role in

the fields of high-temperature ceramics, solid oxide fuel cells and optoelectronics because they possess an excellent combination of thermal [1], electrical [2] and optical properties [3]. Among the rare earth oxide nanoparticles, cerium oxide nanostructures gained wide attention due to their great applicability in the fields of solid oxide fuel cells [4], oxygen gas sensors [5], catalysts, chemical mechanical polishing and ultraviolet shielding [6]. Rare earth ion-doped ceria are potential solid electrolytes due to their higher ionic conductivity, which ensures the possibility of reduction in the operation temperature of SOFCs. Also due to their nontoxic nature and excellent biocompatibility, rare earth ion-doped ceria nanoparticles have been considered as potential material for many biomedical applications [7]. Rare earth ions are ideal for luminescent activators in a variety of host lattices due to their host independent, sharp $4f-4f$ transitions and their ability to produce strong emissions with distinctive colors based on their intra-

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configurational transitions [8–10]. However, the suitability of the activators depends on several structural parameters such as ionic radii, lattice parameter, microstrain and symmetry. Recent studies reveal that relevant properties such as electrical and optical properties were greatly influenced by the lattice strain and symmetry of the crystal [11]. By varying the doping concentration, we can create and tune the defect concentrations such as oxygen ion vacancies that influence the optical and dielectric properties [12]. However, defects hold different roles in different hosts. They act as the emitting center in systems such as zinc oxide (ZnO) [13], while it can act as the PL quenching center in CeO₂ [14]. Another factor is the annealing temperature, which also changes the structural parameters and thus alters the physical properties of the material [15]. Hence, a scientific and systematic investigation of the parameters that affects the structural and physical properties of the material needs particular attention.

In this work, cerium oxide nanocrystals with different doping concentrations of Sm³⁺ were synthesized via oxalate decomposition method. The present study aimed at determining the impact of annealing temperature and doping concentration of Sm³⁺ on the various structural parameters of nanocrystalline ceria. The variations of size, morphology and the optical properties of the nanocrystals with annealing temperature and Sm³⁺ concentration were also discussed in detail.

2 Experimental

2.1 Synthesis

The materials used for the synthesis were cerium nitrate hexahydrate (Ce(NO₃)₃·6H₂O, AR grade, 99.9%, Alfa Aesar), samarium nitrate hexahydrate (Sm(NO₃)₃·6H₂O, AR grade, 99.9%, Alfa Aesar), oxalic acid dehydrate (H₂C₂O₄·2H₂O, 99%, Merck) and ethylene glycol (99%, Merck). For the preparation of CeO₂:Sm³⁺ (Sm³⁺ concentration is 0.5, 1, 1.5, 2, 5, 10, 20 mol%), stoichiometric amounts of samarium nitrate were added to the aqueous solution of cerium nitrate so as to get 0.1 mol/L rare earth nitrate solution. The solution was mixed with equal volume of ethylene glycol together to obtain a homogenous system. Another aqueous solution of 0.15 mol/L oxalic acid was prepared and mixed with equal volume of ethylene glycol. The two solutions were mixed together under vigorous stirring. The whole system was transferred to a microwave oven (2.45 GHz, 700 W), immediately after the formation of a white colloidal solution. The solution was subjected to periodic microwave irradiation for 20 s with a time interval of 10 s. After 10 cycles of irradiation, the precipitated solution was taken from the oven and the precipitates were

collected by filtration. The precipitates obtained were washed many times in double distilled water and then with acetone and finally dried at 60 °C for 24 h.

Controlled thermal decomposition of oxalate precursor was employed to obtain CeO₂:Sm³⁺ nanocrystals. To investigate the changes in the structural and physical properties, the CeO₂:Sm³⁺ nanocrystals were annealed at 400, 600 and 800 °C. The density of the nanocrystals was determined by Archimedes principle and using a specific gravity measurement bottle method.

2.2 Characterization

The crystallinity of the as-prepared samples were determined by X-ray powder diffraction using PANalytical X'Pert Pro diffractometer with CuK_α radiation ($\lambda = 0.154$ nm). The size and morphology of the particles were analyzed by the high-resolution scanning electron microscope JEOL JSM 6020 and the transmission electron microscope JEOL JEM 2100. FTIR spectra were recorded using PerkinElmer Spectrum 400 Spectrometer over the range of 400–4000 cm^{−1}. The photoluminescence analysis was carried out using Horiba Jobin–Yvon Fluoromax 4 spectrofluorometer in the wavelength range 360–650 nm.

3 Results and Discussion

3.1 Structural Characterization

3.1.1 XRD Analysis

The XRD patterns of the pure CeO₂ and CeO₂:Sm³⁺ with 0.5, 1, 1.5, 2, 5, 10, 20 mol% Sm³⁺ annealed at 400, 600 and 800 °C are given in Fig. 1a–c, respectively, and all the XRD patterns were identical with the standard data file of the cubic-structured CeO₂ (ICDD Card No. 655923). It can be found that on increasing the annealing temperature from 400 to 600 °C and further to 800 °C, diffraction peaks of the doped and pure CeO₂ become sharper with increased intensity owing to the increase in the crystalline grain size. XRD diffractograms reveal that all Sm³⁺ ions introduced by doping were successfully incorporated into the crystal lattice of the CeO₂ structure and effectively replaced the Ce⁴⁺ ions without changing the structure. The lattice parameter and crystal volume of the different concentrations of the Sm³⁺-doped CeO₂ annealed at 600 and 800 °C were calculated using the program UnitCellWin. The average crystalline size of the nanocrystals annealed at 600 and 800 °C was calculated using the Debye–Scherrer equation:

$$L = \frac{k\lambda}{\beta \cos \theta}, \quad (1)$$

Fig. 1 X-ray diffractograms of the pure and Sm^{3+} (concentration in mol%)-doped CeO_2 annealed at different temperatures: **a** 400 °C; **b** 600 °C; **c** 800 °C

where L is the crystalline size of the material, k is the shape factor, λ is the wavelength used for the analysis, β is the full width at half maximum of the diffraction peak measured in radian and θ is the angle corresponds to the peak.

3.1.2 Microstructural Study

Studies of nanomaterials need characterization of microstructure with emphasis in the particle size and microstrain. Both factors are influenced by the width of the diffraction peaks and are separated by using a standard Williamson–Hall plot [16] given by the equation:

$$\beta = \beta_{\text{size}} + \beta_{\text{strain}} = \frac{0.9\lambda}{t \cos \theta} + \frac{4(\Delta d) \sin \theta}{d \cos \theta}, \quad (2)$$

where t is the average crystal size, and Δd is the difference of the d spacing corresponding to a typical peak.

The relation in Eq. (2) can be plotted as a linear function that provides microstrain and mean particle size from the slope and the intercept with the y-axis, respectively. The crystalline size calculated by Scherrer equation and W–H plot, lattice parameter, unit cell volume and strain obtained for different doping concentrations and annealing temperatures are detailed in Table 1.

As listed in Table 1, the small differences in the size of the nanoparticles calculated by Scherrer and W–H methods were quite expected because the W–H plots consider both the microstrain and particle size contributions of the broadening in the diffraction peak while Scherrer method considers only the particle size line broadening [17]. The size of the nanoparticles was increased to around two times regardless of the doping concentrations when the annealing temperature rose from 600 to 800 °C. This is due to the fact that an increase in thermal energy promotes the sintering of adjacent particles, which in turn leads to increase in the particle size. Hence, the high surface energy of the particle reduces, and particles become more stable.

Annealing temperature also influences the lattice parameter and strain of the particles. Temperature and

concentration dependence of lattice parameter and microstrain are plotted in Fig. 2. It can be concluded from Fig. 2 that the microstrain and the lattice parameter of the cerium oxide increase with the dopant concentration of Sm^{3+} regardless of the annealing temperature. This is attributed to the higher ionic radii of Sm^{3+} (0.1079 nm) ions compared to that of Ce^{4+} (0.097 nm) ions. When the doping concentration increases, more and more Sm^{3+} are placed in the lattice position of Ce^{4+} owing to the gradual increase in the strain on the particle. Doping with trivalent ions also creates oxygen ion vacancies in the crystal lattice [12]. The introduction of both Sm^{3+} ions and the accompanying oxygen vacancies leads to a distortion of the local symmetry. This causes the change in the Ce–O bond length and the overall lattice parameter. The increase in lattice strain with doping concentration is also supported by the subsequent increase in the unit cell volume in Sm^{3+} -doped CeO_2 . On the other hand, the lattice parameter and the microstrain of the particles decrease on increasing the annealing temperature for all concentrations of Sm^{3+} . It may be due to the stress released at high annealing temperature, which was generated by the doping of higher ionic radii ions [18].

The positions of the diffraction peaks along the plane (111) of the CeO_2 with different concentrations of Sm^{3+} annealed at 600 °C are given in Fig. 3. It is observed that the position of peaks shift toward lower angles and the intensity reduces with increasing concentrations of Sm^{3+} . The shift of peak position is due to the internal tensile stress generated by substitution of Ce^{4+} by the higher ionic radii Sm^{3+} ions [18]. However, the width of the peak is not affected by the increase in the doping concentration revealing that a uniform strain is produced in all directions on the particles by Sm^{3+} substitution [17]. The inset of Fig. 3 shows a magnified image of the diffraction peak at 28.45° for a doping concentration of 20 mol%. It can be seen that diffraction peak corresponding to (111) plane of the CeO_2 splits, which indicates the formation of the secondary phase. Since the (222) plane of the Sm_2O_3 occurred at

Table 1 Crystalline size, lattice parameter, crystal volume and microstrain of pure and Sm³⁺-doped CeO₂ annealed at 600 and 800 °C

Annealing temperature (°C)	Sm ³⁺ concentration (mol%)	2θ (°)	<i>a</i> (Å)	Crystal volume (Å ³)	Strain (10 ^{−4})	Size from HW plot (nm)	Size from Scherrer equation (nm)
600	0	28.65	5.405	157.95	0.818	25	25
	0.5	28.65	5.405	157.95	1.01	24	23
	1	28.648	5.405	157.95	1.54	22	22
	1.5	28.638	5.405	157.95	2.25	25	24
	2	28.58	5.409	158.23	2.34	23	22
	5	28.60	5.413	158.63	2.91	23	21
	10	28.55	5.418	159.02	5.01	20	19
	20	28.45	5.427	159.92	5.46	18	16
800	0	28.75	5.40	157.57	0.285	70	63
	0.5	28.70	5.402	157.63	0.34	67	61
	1	28.68	5.402	157.63	0.495	69	63
	1.5	28.68	5.403	157.76	1.25	77	67
	2	28.67	5.404	157.85	1.57	72	59
	5	28.65	5.411	158.46	1.76	69	56
	10	28.60	5.419	159.14	2.39	46	37
	20	28.53	5.429	160.02	2.62	46	36

Fig. 2 Variations of lattice parameter and microstrain with Sm³⁺ concentration and annealing temperature

28.3 °C (ICDD Card No. 65-3183), it can be assumed that the diffraction peak may be the resultant of the above two planes. The X-ray density ' d_X ' of all samples was calculated using the equation:

$$d_X = \frac{ZM}{NV}, \quad (3)$$

where Z is the number of molecules per unit volume, M is the molecular weight of the sample, V is the unit cell volume and N is the Avogadro's number [19]. The specific surface area (S) was calculated from the X-ray density of the sample (d_X) and diameter of the particle (D) using the following expression:

Fig. 3 XRD peak corresponds to the (111) plane CeO₂ for different doping concentrations of Sm³⁺ and splitting of the peak of Sm³⁺ doping concentration of 20 mol% (inset)

$$S = \frac{6}{d_X D}. \quad (4)$$

The bulk density (d_B) was determined by measuring the specific gravity of the sample. The porosity (P) was calculated using the relation

$$P = 1 - \frac{d_B}{d_X}. \quad (5)$$

The X-ray density, specific surface area, bulk density and porosity are given in Table 2. From the table, we can suggest that the X-ray density of the Sm³⁺-doped CeO₂

Table 2 X-ray density, specific surface area, bulk density and porosity of pure and Sm^{3+} -doped CeO_2 annealed at 600 and 800 °C

Annealing Temperature (°C)	Sm^{3+} (%)	X-ray density (g/cm^3)	Specific surface area (m^2/gm)	Bulk density (g/cm^3)	Porosity
600	0	7.24	33.2	5.77	0.20
	0.5	7.24	36	5.64	0.22
	1	7.24	37.7	5.20	0.28
	1.5	7.24	34.5	5.15	0.29
	2	7.23	37.7	5.10	0.30
	5	7.21	39.6	5.04	0.30
	10	7.20	43.9	4.89	0.32
	20	7.16	52.3	4.57	0.36
800	0	7.25	11.8	6.28	0.13
	0.5	7.25	12.3	6.2	0.14
	1	7.25	12	6.30	0.13
	1.5	7.25	10.8	6.25	0.14
	2	7.22	11.5	6.22	0.14
	5	7.22	12	6.2	0.14
	10	7.19	18.1	6.18	0.14
	20	7.15	18.2	5.6	0.22

nanocrystals decreases with an increase in the concentration of Sm^{3+} . This result is quite expected because density is inversely proportional to the volume of the crystal. As the dopant increases, the lattice parameter also increases, which leads to the expansion of the crystal. The particle size is the critical parameter that determines the specific surface area of the crystal, and hence, the surface area is high for higher concentrations of samarium due to the small particle size. It is found that the bulk density of the nanocrystals decrease with the increase in doping concentration, whereas it increases with the annealing temperature. This may be due to the presence of more number of defects and oxygen ion vacancies introduced during doping [20, 21]. A higher annealing temperature results in a more ordered arrangement of crystallites and leads to an increase in the bulk density. However, the porosity of the material is found to increase with the doping concentration and decreases when the annealing temperature is raised to 800 °C.

3.1.3 SEM Analysis

A detailed microstructural and morphological investigation of the $\text{CeO}_2:\text{Sm}^{3+}$ was carried out using SEM analysis. SEM images of the pure CeO_2 annealed at 400, 600 and 800 °C are given in Fig. 4a, c, e, respectively, while $\text{CeO}_2:\text{Sm}^{3+}$ (doping concentration of 1 mol%) annealed at the above temperatures is given in Fig. 4b, d, f. It can be observed from Fig. 4a, b that the samples annealed at 400 °C exhibit plate-like morphology with smooth surfaces irrespective of the doping of Sm^{3+} ions. However, the size

of the plates was in the micro- to nano-regime. From Fig. 4c, d, it can be observed that on increasing the annealing temperature to 600 °C, the plate-like structures were broken into small pieces while losing their uniform morphology. Hence, it can be concluded that the plate-like morphology is due to the aggregation of the small particles occurred during the synthesis. The primary reason of the oriented aggregation is due to the involvement of the ethylene glycol used in the synthesis. Due to the greater viscosity of the ethylene glycol, the nanocrystals are kinetically slower, find the low-energy configuration interface and form oriented assemblies [22]. Similar kind of formation of aggregated nanocrystals was already reported for oxalates [23]. The plate-like morphology is sustained even at a temperature of 400 °C but destroyed at 600 °C. Figure 4e, f reveals that particle size increases at higher temperatures due to the sintering mechanism.

3.1.4 TEM Analysis

For the detailed investigation of the size and structure of the particles, transmission electron microscopic image of the pure CeO_2 and $\text{CeO}_2:\text{Sm}^{3+}$ (doping concentration of 1 mol%) annealed at 400 °C was taken and is given in Fig. 5a, b, respectively. The samples for the analysis were prepared by ultrasonication method in isopropyl alcohol for 1 h to get a dispersed solution for imaging. Figure 5a, b clearly demonstrates that the platelet morphology of the samples is due to the aggregation of the nanocrystals of an average size less than 20 nm. The nanocrystals aggregated to form micro-sized structures, which is in agreement with

Fig. 4 SEM images of the crystals: **a** CeO₂ annealed at 400 °C; **b** CeO₂ doped with 1 mol% Sm³⁺ annealed at 400 °C; **c** CeO₂ annealed at 600 °C; **d** CeO₂ doped with 1 mol% Sm³⁺ annealed at 600 °C; **e** CeO₂ annealed at 800 °C; **f** CeO₂ doped with 1 mol% Sm³⁺ annealed at 800 °C

Fig. 5 TEM images of the crystals: **a** pure CeO₂ annealed at 400 °C; **b** CeO₂ doped with 1 mol% Sm³⁺ annealed at 400 °C; **c** HRTEM and SAED pattern of pure CeO₂ annealed at 400 °C; **d** pure CeO₂ annealed at 600 °C

the conclusions of the SEM analysis. The HRTEM image and SAED pattern given in Fig. 5c indicate the low crystallinity of the sample annealed at 400 °C. Figure 5d shows the TEM image of the CeO₂ annealed at 600 °C, which confirms that the plate-like structure due to the oriented aggregation completely vanished and uniform spherical nanocrystals of size 15–20 nm were obtained by the annealing at 600 °C. Hence, it is suggested that thermal decomposition of oxalate is an effective and simple method for synthesizing less agglomerated uniform Sm³⁺-doped cerium oxide nanocrystals compared to other methods [24, 25].

3.1.5 FTIR Analysis

Fourier transform infrared spectra of the CeO₂ nanocrystals annealed at 400, 600 and 800 °C are given in Fig. 6, and the inset shows the enlarged view of the low intensity peaks. The spectrum of CeO₂ nanocrystals annealed at

400 °C exhibits a broad band in the region of 3000–3500 cm^{−1}, which can be attributed to O–H stretching of water molecules [26]. The band located at about 1630 cm^{−1} is due to the combined effect of the H–O–H from phys-absorbed water molecules and the O–C–O stretching band [27]. The presence of the bidentate carbonate species was identified by the peaks at 1530 and 1317 cm^{−1}, which are usual in ceria due to the interaction with atmospheric carbon dioxide [28]. The spectra reveal that all the absorption peaks due to water molecules and carbonate groups gradually disappeared on increasing the annealing temperature to 600 and further up to 800 °C.

3.2 Optical Characterizations

Fluorescence analysis was performed to investigate the dependence of luminescence characteristics of the crystals with temperature and doping concentrations. Luminescence excitation spectra of the CeO₂ with different

Fig. 6 FTIR spectra of the 5 mol% Sm^{3+} -doped CeO_2 annealed at 400, 600 and 800 °C (inset is the enlarged view of the spectra)

Fig. 7 Excitation spectra of Sm^{3+} -doped CeO_2 annealed at 400, 600 and 800 °C

concentrations of Sm^{3+} synthesized at the annealing temperatures of 400, 600 and 800 °C are shown in Fig. 7. The excitation spectra were obtained by monitoring the prominent emission of Sm^{3+} at the wavelength 573 nm. The spectra exhibit a wide and strong excitation band due to the charge transfer from O^{2-} to Ce^{4+} in the wavelength region 300–370 nm [18, 29]. It is found that the charge transfer band shifts to a lower energy when the annealing temperature increases. This redshift is related to the effect of the environmental factor, which depends on the

Fig. 8 Emission spectra of Sm^{3+} -doped CeO_2 annealed at 400, 600 and 800 °C

structural symmetry, unit cell parameter and refractive index of the crystal [30]. Hence, the annealing temperature directly influences the environmental factor and thus the position of the charge transfer band. It is also evident that the intensity of the emission at 573 nm is increased when the concentration of Sm^{3+} increased from 0.5 to 1 mol%. The intensity of the excitation band decreases for higher concentration, which reveals that the emission at 573 nm is quenched due to the higher concentrations of the Sm^{3+} ions. The luminescence is completely quenched above the 5 mol% doping concentration. There are many reports that the defect sites also play a major role in the quenching mechanism by offering a nonradiative transfer route for electrons to relax to the ground state [18]. At higher Sm^{3+} concentrations, the distance between the ions become shorter, which results in an effective transfer of energy to neighboring ions and to a longer extent. Presence of defect sites in the path of the energy migration promotes the nonradiative relaxation, and this will lead to a decrease in luminous intensity.

Photoluminescence emission spectra of the pure and doped CeO_2 nanocrystals are shown in Fig. 8, which shows that the annealing temperature does not affect the position of the emission peaks. The emission characteristics of Sm^{3+} strongly depend on the symmetric behavior of the crystal lattice. Sm^{3+} ions have four emissions in the visible region at 573, 615, 648 and 705 nm corresponding to the transition from $^4G_{5/2}$ to $^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$ and $^6H_{11/2}$,

respectively [31]. Of the four emission transitions, the first two are magnetic dipole allowed transitions [32], while the transitions from $^4G_{5/2}$ to $^6H_{9/2}$ and $^6H_{11/2}$ are electric dipole transitions. In CeO_2 crystal lattice, the site occupied by Ce^{4+} has ideally Oh symmetry with eightfold oxygen coordination. According to the Judd–Ofelt theory, the electric dipole transitions are not allowed in the presence of inversion symmetry, but magnetic dipole transitions are independent of the site symmetry of the surrounding lattice, and hence, the magnetic dipole transitions dominate the spectra of crystals having inversion symmetry [23]. Thus, the emission spectra of the Sm^{3+} -doped cerium oxide exhibit two strong peaks at 573 and 615 nm, and the transition $^4G_{5/2} \rightarrow ^6H_{5/2}$ possesses the maximum intensity.

4 Conclusions

CeO_2 nanocrystals with different doping concentrations of Sm^{3+} between 0.5 and 20 mol% were successfully synthesized via thermal decomposition of oxalate precursor. X-ray diffraction analysis reveals that Sm^{3+} -doped CeO_2 exhibits the same structure and phase as that of cubic-structured CeO_2 . Phase of the Sm_2O_3 was observed in the XRD pattern of the 20 mol% Sm^{3+} -doped CeO_2 , which implies the solubility limit of the Sm^{3+} . Extra strain is created by the doping of large ionic radii element, which leads to the increase in the lattice parameter and expansion of the crystal volume. Detailed analysis revealed that an increase in the annealing temperature leads to the reduction in strain exhibited by the crystal. The doping and annealing temperature also influence on the structural parameters such as X-ray density, surface area, bulk density and porosity. SEM images of the crystals reveal that uniform-sized nanoparticles were formed by the thermal decomposition of oxalate precursor. At lower temperature, the nanocrystals tend to aggregate together to form microparticles. Homogenous nanocrystals with size 20 nm were obtained on annealing at 600 °C. TEM analysis result of the crystals confirms the nanocrystalline nature of the $\text{CeO}_2:\text{Sm}^{3+}$ and supports the suggestions made by the XRD and SEM analysis. Optical studies revealed that the luminescence behavior of the nanocrystals is influenced by the structure, temperature and concentration. Maximum luminescence intensity was achieved for Sm^{3+} -doping concentration of 1 mol%. Hence, the size of the nanocrystal and efficiency of the emission can be effectively tuned by optimizing the annealing temperature and doping concentration for specific applications.

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