Plasma-electrochemical synthesis of europium doped cerium oxide nanoparticles

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Abstract In the present study, a plasma-electrochemical method was demonstrated for the synthesis of europium doped ceria nanoparticles. Ce(NO$_3$)$_3$·6H$_2$O and Eu(NO$_3$)$_3$·5H$_2$O were used as the starting materials and being dissolved in the distilled water as the electrolyte solution. The plasma-liquid interaction process was in-situ investigated by an optical emission spectroscopy, and the obtained products were characterized by complementary analytical methods. Results showed that crystalline cubic CeO$_2$:Eu$^{3+}$ nanoparticles were successfully obtained, with a particle size in the range from 30 to 60 nm. The crystal structure didn’t change during the calcination at a temperature from 400°C to 1000°C, with the average crystallite size being estimated to be 52 nm at 1000°C. Eu$^{3+}$ ions were shown to be effectively and uniformly doped into the CeO$_2$ lattices. As a result, the obtained nanophosphors emit apparent red color under the UV irradiation, which can be easily observed by naked eye. The photoluminescence spectrum further proves the downshift behavior of the obtained products, where characteristic $^5$D$_0$→$^7$F$_{1,2,3}$ transitions of Eu$^{3+}$ ions had been detected. Due to the simple, flexible and environmental friendly process, this plasma-electrochemical method should have great potential for the synthesis of a series of nanophosphors, especially for bio-application purpose.

Keywords plasma-electrochemical method, europium doped ceria, rare earth nanoparticles, photoluminescence

1 Introduction

As the most abundant rare earth metal which comprises about 0.0046% by weight in the Earth’s crust, cerium (Ce) and cerium-based compounds have historically gained great interests from different fields [1]. Among them CeO$_2$ has received much attention due to the low reduction potential and coexistence of Ce$^{3+}$/Ce$^{4+}$ on its surfaces. The interchangeability of the valence states (4+ and 3+) of the cerium ions leads to oxygen vacancies within the CeO$_2$. In such a case, electrons are regarded as small polarons, and the motion of the electrons is imagined as a thermally mediated hopping mechanism [2]. This property makes CeO$_2$ an attractive material for oxide ion conductors, and remarkable applications ranging from catalysts, fuel cells, host material to electrochemical devices, antioxidants and gas sensors have been explored [3]. Beside the use in the aforementioned fields, the application of CeO$_2$ nanoparticles in the life science industry has been researched over the last years. The interest in this field started in 2006 when the first in vitro cytotoxicity tests for nanoparticles concluded that ceria has a low toxic effect [4]. The redox reaction cycle between the two oxidation states of the cerium ions has a good similarity to antioxidant enzymes [5]. However, for the use in cell imaging or as light source for cancer treatment, the emission of CeO$_2$ itself is very weak. Suitable doping activators in CeO$_2$ matrix are needed to achieve good emission performance. Recently, europium doped cerium oxides have been considered as promising luminous lanthanide complexes. It is well-known that europium has a strong red emission and can be excited from ultraviolet to visible light. An optimal spectral overlap is found to exist between the charge transfer band of CeO$_2$ and the 4f-4f intra configurational transitions of Eu$^{3+}$ ions. The absence of electrons in the 4f shell makes CeO$_2$ an ideal host material for europium. By
doping Eu$^{3+}$ ions into CeO$_2$ host, it can encourage effective energy transfer from the Ce$^{4+}$-O$^{2-}$ host to Eu$^{3+}$ ions and greatly enhance the luminescent properties [6]. Moreover, since the ionic radius of Eu$^{3+}$ (0.1066 nm) is close to that of Ce$^{3+}$ (0.1143 nm) and Ce$^{4+}$ (0.097 nm), it favors extensive solubility of Eu$^{3+}$ within the ceria lattice [7].

Owing to the low dimensionality and large surface area, nanoparticles usually exhibit unique properties that differ considerably from bulk materials. The decrease of the CeO$_2$ size can prompt the formation of oxygen vacancies, leading to an improved electron mobility. Once reduced to the nm-level, these oxygen vacancies can alter the electronic and valence arrangement. In this case, the substitution of Ce$^{4+}$/Ce$^{3+}$ by Eu$^{3+}$ will greatly enhance the emission characteristics of CeO$_2$ particles, since it is more convenient for energy transfer between Eu$^{3+}$ and the redox pair Ce$^{4+}$ and Ce$^{3+}$ oxidation states. Besides, nano-sized particles have the possibility to be transported through tissues and even cells. If CeO$_2$:Eu$^{3+}$ nanoparticles were engineered with appropriate proteins, they can be used for bio-imaging or bio-labeling purpose. This in combination with their intrinsic low toxicity, good biocompatibility, high chemical stability and excellent luminescent property further prompt their applications in the life science field.

Despite the promising perspective of CeO$_2$:Eu$^{3+}$ nanoparticles for bio-applications, currently it is still a challenge to prepare high purity crystalline products in a simple and environmentally friendly manner. Conventional wet chemistry methods require the usage of extra chemicals and pretreatment of the solution. Meanwhile, stabilizers or surfactants which used to limit particle growth are commonly needed. As a result, purification procedures like repeated washing and drying are need to get rid of impurities [8]. On top of that, these methods usually involve toxic chemicals, which may cause unexpected influence on biosystems or on the environment. As to solid-state reaction methods, they are almost operated at sintering temperatures as high as 1500°C–1600°C, with the grain size of the obtained powders on the order of 5–20 µm. Thus, to obtain nano-sized CeO$_2$:Eu$^{3+}$ phosphors for bio-application uses, the powders must be repeatedly ground and milled. Due to the introduction of additional defects during the mechanical procedures, it can greatly reduce the luminescence efficiency of the products.

As a partially ionized gas consisting of electrons, ions, photons, molecules and excited species, plasma-based method can be a promising solution. Due to the existence of abundant reactive species, some thermodynamically unfavorable reactions can take place easily in plasmas under mild conditions [9]. In recent years, plasma-assisted nanofabrication has attracted considerable interests, especially plasma-based liquid electrochemical synthesis. It is well-known that liquid has a larger density than gas. The generation plasma in liquid will have additional confinements, resulting in a higher density of reactive species. Moreover, heat can be dissipated immediately in liquid, ensuring a rather low system temperature as well as limited particle nucleation and growth rate. Therefore, the obtained nanoparticles have smaller sizes and narrower size distributions [10–12].

In the present work, a plasma-electrochemical method was introduced for the synthesis of CeO$_2$:Eu$^{3+}$ nanoparticles. The goal is to explore a simple and green way to prepare rare-earth element doped cerium oxide without involving any toxic chemicals and complex purification processes. Because of the high reactivity of plasma, the plasma-liquid interaction in the aqueous layer can form active radicals like OH, O and H from water molecules. This can avoid the usage of extra hydrolyzing agents, stabilizers and surfactants, which also favors the application of the generated products in bio-related fields.

2 Experimental

In this study all experiments were carried out in a specially-designed plasma reactor (Fig. 1), which has been successfully used to synthesize yttrium oxides and TiN nanoparticles [13,14]. Detailed information of the experimental setup can be referred to the above researches. The electrolyte solution was prepared by dissolving Ce(NO$_3$)$_3$·6H$_2$O (434.22 g/mol, Sigma Aldrich) and Eu(NO$_3$)$_3$·5H$_2$O (428.06 g/mol, Sigma Aldrich) in demineralized H$_2$O to obtain a total Eu/Ce concentration of 0.05 mol/L. The ratio of europium to cerium was varied...
between 0 and 10%. In a typical procedure, 10 mL solution was filled in the quartz microplasma reactor. A capillary (I.D. = 318 µm, O.D. = 1.6 mm) made from stainless steel was used as a cathode and being placed 1 mm above the liquid surface. A platinum disk was immersed in the liquid as the counter electrode. To ignite and sustain the plasma, both electrodes were connected to a negatively biased DC power supply (Matsusada Precision, Model AU-10R30), with the anode electrode being grounded. In each operation, a continuous argon flow of 100 sccm was coupled into the capillary as the plasma gas. It was flowed into the sealed reactor for several minutes before the reaction to get rid of impurities like oxygen and nitrogen. The gas flow rate was controlled by a mass flow controller. During the reaction, no external heating was applied. Experimental values of the plasma current, voltage and power can be automatically recorded using a LabVIEW based program. After the plasma-electrochemical reactions, the solution was centrifuged for 10 min at 4000/s to obtain the products, which were then dried at 50°C to get solid powders. Afterwards, these powders were furtherly heat-treated at different temperatures to get the oxide product, and they were carefully scraped from the plate for complementary characterization.

The optical emission spectra were recorded using an HR2000 + ES spectrometer (Ocean Optics, Inc.). This non-intrusive technique helps to identify the existed reactive species in the complex plasma-assisted process, and gives valuable information of the excited states of the short-live radicals. The emitted light during the plasma-liquid interactions were collected by an optical fiber fixed which was fixed 20 mm from the electrodes axis. The energy dispersive X-ray spectroscopy (EDX) characterization was performed with a Phenom ProX (Phenom World), with a silicon drift EDX detector to examine the element distribution (Sapphire DPP-2). Transmission electron microscopy (TEM) and high-resolution TEM images were obtained using a FEI Tecnai 20 (Sphera) microscopy operated with a 200 kV LaB6 filament. The X-ray diffraction patterns of the synthesized particles were obtained with a Rigaku Powder Diffractometer using Cu-K\textsubscript{α1} radiation (K\textsubscript{α} = 1.54056 Å). The scans were recorded in a 2θ step of 0.02° with a dwell time of 20 s in each step. The Raman spectroscopy measurements were taken with a laser diode emitting light at 632 nm and an 1800 lines/mm grating. Si wafer was used to calibrate the Raman system by the prominent peak at the wavelength of 520.6 cm\textsuperscript{-1}, followed by the measurement of solid samples on a glass substrate. The measurements were performed at laser power density of 1 mW. The XPS measurements were carried out with a Thermo Scientific K-Alpha X-ray photoelectrons spectroscopy, equipped with a monochromatic small-spot X-ray source and a 180° double focusing hemispherical analyzer with a 128-channel detector. Spectra were obtained using an aluminium anode (Al K\textsubscript{α} = 1486.6 eV) operated at 72 W and a spot size of 400 µm. Survey scans were measured at a constant pass energy of 200 eV and region scans at 50 eV. The photoluminescence measurements were performed at room temperature on a luminescence spectrometer (Perkin Elmer, Model LS-50B) using 360 nm wavelength as the excitation wavelength. The samples were prepared by pressing solid powders into a hole on the sample holder with a glass slide.

3 Results and discussion

Time-evolution images of the plasma-treated electrolyte solution are presented in Fig. 2. It is shown that the clear and colorless solution gradually turns into slightly white and semitransparent after plasma operation for 1 h, in which white floccules are formed. This suggests chemical reactions can be induced by the plasma-assisted process, without the addition of extra chemicals. As the plasma-driven process continues, the semitransparent solution becomes increasingly turbid. One can observe that more and more white floccules were generated and deposited from the electrolyte. The solution becomes totally creamy white after approximately 4 h.

In addition to the visual-appearance of the plasma-treated solution, we also investigated the optical emission spectra of the plasma-liquid interaction process. In this research, both the emission spectra of pure argon plasma as well as argon plasma interacting with the electrolyte solution were acquired, as shown in Fig. 3. For the pure argon case, the spectrum is merely composed of emission lines in the red/near-infrared spectral region (680–950 nm), which can be attributed to the argon 3p’ 4p-3p’ 4s transitions. By contrast, when interacting with the liquid

![Fig. 2](image-url) The images of the electrolyte solution treated by plasma for (a) 0 h, (b) 1 h, (c) 2 h, (d) 3 h and (e) 4 h
solution, new spectral features of the neutral hydrogen line at $\lambda = 656$ nm (H$_\alpha$) as well as the molecular bands of the OH radicals at $\lambda = 310$ nm (the 3064 Å system) are observed, suggesting the splitting of H$_2$O molecules under the plasma impact [15].

In the studied reactor configuration, the capillary tube was negatively biased with respect to the platinum electrode. Owing to the external electrical field, plasma electrons were driven toward the electrolyte surface to collide with water molecules. These energetic electrons can dissociate water molecules to generate H and OH radicals, which have been detected by the OES spectra Eq. (1). Meanwhile, metastable OH radicals are highly reactive. They will combine with plasma electrons to form OH$^-$ in the liquid Eq. (2). On the other hand, the equilibrium solubilities of the studied lanthanide hydroxides are rather low ($\sim 10^{-7}$ g/mL). Both the europium ions and the cerium ions are easily hydrolyzed to form colloidal deposits from the electrolyte solution Eq. (3). This can be reflected by the images of the electrolyte solution under plasma treatment at different times (Fig. 2).

$$
\begin{align*}
H_2O + e^- & \rightarrow H^+ + OH^- \quad (1) \\
OH^+ + e^- & \rightarrow OH^- \quad (2) \\
Ce^{3+} + Eu^{3+} + 3OH^- & \rightarrow [Ce(OH)_3 : Eu] \downarrow \quad (3)
\end{align*}
$$

The elemental mapping over a random area of the Eu$^{3+}$ doped CeO$_2$ samples reveals the existence of Ce, O and Eu elements, without the appearance of any other impurities (Figs. 4(a–d)). Moreover, Eu shows a homogeneous distribution among the Ce and O element, suggesting it has been uniformly incorporated into the CeO$_2$ nanoparticles. The EDX analysis further confirms this result, where strong Ce and O as well as low intensity Eu signals are observed, and no extra impurities are detected (Fig. 4(e)).

Figure 5(a) shows the XRD patterns of CeO$_2$:Eu$^{3+}$ nanoparticles with the europium doping concentration varying from 2% to 10%. In general, all the diffraction peaks locate at the same positions and well match with the cubic fluorite structure of CeO$_2$ (JCPDS #81-0792) [16]. No peaks of Eu, Eu$_2$O$_3$ and Eu(OH)$_3$ are detected, indicating that europium have been effectively entered into the CeO$_2$ lattice. However, compared with pure CeO$_2$, the diffraction peaks of Eu doped CeO$_2$ nanoparticles shift to a larger 2$\theta$ value, which can be observed more clearly in the range from 26$^\circ$ to 34$^\circ$. This is attributable to the doping of europium ions into the host matrix, where europium ions have a larger ionic radius ($r = 1.1206$ Å) than cerium ions ($r = 1.11$ Å), leading to the lattice expansion [17]. The influence of the annealing temperature is also investigated (Fig. 5(b)). For powders dried at room temperature, only three broad peaks with very low intensities at 28$^\circ$, 47$^\circ$ and 56$^\circ$ are visible, suggesting they are poorly crystallized. In the temperature range from 400$^\circ$C to 1000$^\circ$C, the peaks show an apparent narrowing trend, inferring an enhanced crystallite growth with the increased temperature. Meanwhile, all peaks are characteristic diffractions of the cubic fluorite structure, suggesting no structural change during the calcination process. The average crystalline size ($d$) of the nanoparticles annealed at 1000$^\circ$C is estimated from the highest intensity peak (111) at 28$^\circ$ using the Scherrer formula

$$d = \frac{K\lambda}{\beta\cos \theta},$$

where $K$ is the shape factor, which is 0.89 for the cubic fluorite structure of ceria; $\lambda$ the wavelength of the X-rays (1.54056 Å); $\beta$ is the line broadening at half maximum peak intensity in radians; $\theta$ is the Bragg angle [18]. It is calculated that the crystallite size is 52.2 nm at the studied condition.
Figures 6(a,b) show representative TEM images of the CeO$_2$:Eu$^{3+}$ products. Nano-sized particles of irregular shapes were observed, with measured size ranging from 30 to 60 nm. Due to the calcination, they are partially aggregated together. It is noteworthy that this technique allows the preparation of nanoparticles within 60 nm at 1000°C, which are much smaller compared with other physical or chemical methods that without stabilizers or surfactants (those are mostly larger than 100 nm and may reach micro-size level) [19,20]. Since conventional wet chemistry methods use supersaturated alkali precipitants, cerium hydroxides easily nucleate and grow to a large extent due to the vigorous hydrolyzing reactions. By contrast, in this method OH$^-$ are smoothly generated from water molecules to deposit ultra-small floccules in a mild condition, avoiding overgrowth of the deposits. The atomic-level particle structure was also examined by the high-resolution image, as shown in Fig. 6(c). Clear lattice fringes are observed, implying the crystalline nature of the synthesized particles. This was supported by the inserted FFT image as well as by the SAED image, in which diffraction rings arising from the (111), (200), (220), and (311) lattice planes are detected.

Raman analysis was performed to provide a structural fingerprint of CeO$_2$ nanoparticles with Eu$^{3+}$ doping. Figure 7 shows the raman spectra of CeO$_2$ nanoparticles with (red one) and without (black one) Eu$^{3+}$ doping. For the pure CeO$_2$ nanoparticles, a significant band located at 465 cm$^{-1}$ is observed, which is ascribed to the first order scattering of CeO$_2$ nanoparticles (F$_{2g}$ mode). This band is
caused by the stretching of the Ce–O–Ce symmetric vibration, where Ce and O are 8-fold and 4-fold coordinated [21]. Additionally, a number of bands ranging from 250 to 1400 cm$^{-1}$ that originated from the second order scattering are also detected. These bands belong to different phonon symmetry modes. By contrast, for the Eu$^{3+}$ doped CeO$_2$ nanoparticles, several new bands emanated from 1150 to 1850 cm$^{-1}$ are detected, suggesting the chemical bonds and symmetric vibration are changed. This is entirely due to the incorporation of Eu$^{3+}$ into the CeO$_2$ matrix. Same phenomenon has been reported by Burger et al., where Eu$^{3+}$ was doped into yttria by wet chemical routes with combustion and coprecipitation techniques [22]. The Raman results further confirms the successful synthesis of CeO$_2$ nanoparticles as well as the doping of Eu$^{3+}$ into the CeO$_2$ matrix by the plasma-induced technique.

To further investigate the chemical compositions and binding information of the products, XPS characterization is employed for both Eu$^{3+}$ doped and undoped CeO$_2$ nanoparticles (Fig. 8). It is clearly shown that both samples consist of Ce and O. However, the peaks corresponding to Eu 4s and Eu 3d are not visible in the undoped ceria spectrum but are in the doped spectrum (~400 and 1135 eV). The result is in consistent with the EDX result, reconfirming the presence of europium in ceria. To get more details about the element states, high resolution spectra of Ce 3d, Eu 3d and O 1s are presented in Figs. 8(b–d). For the Ce 3d, the spin-orbital-splitting of the 3d$_{5/2}$ (878–898 eV) and 3d$_{3/2}$ (898–920 eV) are clearly visible. Each doublet is further split by multiple splitting, representing different 4f configurations in the photoemission initial and the final states. The peaks at 898 and 916.7 eV are indexed to the Ce$^{4+}$ 3d$_{3/2}$ and Ce$^{4+}$ 3d$_{5/2}$ contributions, while the peaks situated at 882.8 and 901.4 eV correspond to the binding energy of Ce$^{3+}$ 3d$_{3/2}$ and Ce$^{3+}$ 3d$_{5/2}$. Therefore, it demonstrates the existence of a small amount of Ce$^{3+}$ at the surface, which is well-known for CeO$_2$ nanoparticles [23]. The results are characteristic spectral features of ceria, and can be taken as evidence of the formation of CeO$_2$ nanoparticles [24]. The Eu 3d binding at 1163 and 1134 eV are assigned to the Eu$^{3+}$ 3d$_{5/2}$ and Eu$^{3+}$ 3d$_{3/2}$, respectively, indicating the formation of Eu–O bonds from europium ions which exist in the form of trivalent ions (Eu$^{3+}$). This revealed that part of europium ions form Eu$_2$O$_3$ within the nanophosphors. Spectral decomposition of O 1s bands further confirms the above findings. The most prominent peak at 529.1 eV as well as the associated low intensity peak at 530.5 eV are typical O–Ce bonds that widely existed in CeO$_2$ nanoparticles [25]. Moreover, as reported by Yuan et al., two additional peaks at 532.2 and 533.4 eV are due to O–Eu binding as well as the oxide impurities such as O–C compounds or O–H species [26].

Figure 9 shows representative emission spectra of CeO$_2$ nanoparticles without/with 4% Eu doping. In Fig. 9(a), a broad emission bands are observed at around 390 and 415 nm when irradiated at 300 nm, which are characteristic spectral features of CeO$_2$, in consistent with reference [27]. Meanwhile, the emission bands located between 340 and 500 nm are originated from the defect states of CeO$_2$, such as oxygen vacancies between Ce 4f state to O 2p state [28]. As to the emission spectrum of Eu$^{3+}$ doped CeO$_2$ nanophosphors, two most intensive peaks situated at 589 and 612 nm are indexed to the $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transition of Eu$^{3+}$ ions, respectively. The $^5D_0 \rightarrow ^7F_1$ transition is known as the parity-allowed magnetic dipole
transition and is insensitive to the crystal field environment, while the $^5D_0 \rightarrow ^7F_2$ transition originates from the electronic dipole transition and being hypersensitive to the local symmetry around the Eu$^{3+}$ ions. According to the Judd-Ofelt theory, the incorporation of Eu$^{3+}$ ions into CeO$_2$ host would perturb their structure. At low doping concentrations, the Eu$^{3+}$ ions mainly enter into the lattice with inversion symmetry. With the increased Eu$^{3+}$ doping, they can replace Ce$^{4+}$ and create symmetry distortions to cause the electric dipole transitions [6]. In the present case,
the $^5D_0 \rightarrow ^7F_1$ transition is found to be higher than the $D_0 \rightarrow ^7F_2$ transitions, indicating that most of the Eu$^{3+}$ ions go into the lattice instead of occupying the Ce$^{4+}$ sites. This agrees with the study of Shi et al., where the $^5D_0 \rightarrow ^7F_1$ transition is stronger than other transitions at the 4% Eu$^{3+}$ doping concentration [17]. In addition, an optical photograph of the nanophosphor under the same UV wavelength is also shown in the inset of Fig. 9(b). Apparent red fluorescent light is clearly visible from the CeO$_2$:Eu$^{3+}$ sample by the naked-eye, confirming their downshifting nature.

Currently a series of methods have been developed for the synthesis of europium doped ceria nanoparticles. Table 1 gives a comparison of the main parameters between the plasma-electrochemical technical and other conventional methods to show their pros and cons. Compared to the existing methods, it is indicated that this plasma-electrochemical method is relatively simpler. High purity CeO$_2$:Eu$^{3+}$ nanoparticles can be fabricated via a two-step manner: plasma electrodeposition reactions followed by a calcination process. Time and energy consuming pre/post-treatment procedures such as milling, pre-heating or organic washing are not needed. Moreover, this approach avoids the usage of any toxic chemicals, making it of great promising and interest to various applications, especially for the life science field.

4 Conclusions

In the present study, we have successfully synthesized europium doped ceria nanophosphors by a plasma-electrochemical method, without the use of any toxic chemicals as well as complex purification procedures. Complementary characterizations were carried out to study the plasma-liquid interaction process as well as the obtained products. Results showed high purity crystalline CeO$_2$:Eu$^{3+}$ nanoparticles of the cubic fluorite structure were obtained, with an averaged crystallite size being calculated to be 52.2 nm at the calcination temperature of 1000°C. Moreover, europium ions were proved to be effectively incorporated into the CeO$_2$ matrix. The obtained nanophosphors exhibited clear downshifting behaviour, where the $^5D_0 \rightarrow ^7F_1$ transition was found to be higher than the $D_0 \rightarrow ^7F_2$ transitions.

The combination of highly reactive plasma species, non-equilibrium state, milli-scale reactor and low-temperature operation may offer alternative routes for thermodynamically unfavorable reactions to take place under mild conditions. In terms of nanofabrication, plasma-based synthesis allows the production of nanostructures more efficiently in a well-controlled and green way. The unique kinetics of nonthermal plasma can lead to a fast nucleation but a slow crystal growth, in comparison to the traditional wet chemistry methods. Moreover, due to the high flexibility in choosing precursors, this method can produce a broad range of nanomaterials, such as metal nanoparticles, oxides, nitrides, nanoalloys as well as core/shell nanostructures. With the significant progress being achieved in the plasma-electrochemical nanofabrication field, it can be expected that this technique should have great potential

| Methods                      | Step | Extra toxic chemicals | Temperature/°C | Size/nm | Pre/post treatment       | Remark                        | Ref.   |
|------------------------------|------|-----------------------|---------------|--------|-------------------------|-------------------------------|-------|
| Plasma-assisted              | 2    | None                  | 400–1000      | 20–60  | Centrifugation           | Eu$_2$O$_3$ as the raw material | [29]   |
| Coprecipitation-calcination  | 4    | HNO$_3$              | 1300          | Micro-powder | Centrifugation Washing |                               |       |
| Hydrothermal method          | 4    | NH$_4$OH             | 180–450       | 300–400 | Stirring                | Centrifugation Washing       | [23]   |
| Ultrasonic spray pyrolysis   | 5    | C$_2$H$_5$O$_2$      | 1000          | 40–80  | Dissolution             | Centrifugation Washing       | [30]   |
| Micro-emulsion reaction method| 6    | C$_3$H$_7$O$_7$      | 1000          | 30–55 (surfactant needed) | Milling | Washing | Stirring | Evaporation | CeO$_2$ as the raw material | [31]   |
| Sol-gel method               | 4    | C$_6$H$_9$O$_7$      | 400–900       | 15–55  | Milling | Pre-fire | Stirring | Complex procedures |                               | [32]   |
| Solvothermal process         | 3    | C$_6$H$_9$O$_7$      | 500–900       | 5–27   | Pre-heating | Stirring | Washing | Long reaction time |                               | [33]   |
for the production of nanophosphors in a simple, flexible and environmentally friendly manner.

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