Synthesis and microstructure of Al$_2$O$_3$ aerogel composite induced by different transition/lanthanide metal ions

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Abstract

The study of the influence of different substances introduced on the same matrix will provide a good guide for the construction of materials with good properties. A series of transitions/lanthanides metal ions doped or co-doped Al$_2$O$_3$ aerogel materials with three-dimensional nano porous structure were fabricated by a simple and facile modified sol-gel method. The effect of different transitions/lanthanides metal ions on the microstructure, textural properties, and luminescence properties of Al$_2$O$_3$ aerogels were investigated. By co-doping the Al$_2$O$_3$ aerogel matrix with Eu$^{3+}$ and Tb$^{3+}$, we fabricated Al$_2$O$_3$ aerogel luminescent materials with tunable color emissions under UV excitation. The characterization results showed that the microscopic morphology of these aerogels induced by transitions/lanthanides metal ions were obviously different. Interestingly, Al$_2$O$_3$-Eu/Tb (III) and Al$_2$O$_3$-Tb/Ce (III) aerogels exhibited a special flower-like structure. It is hoped that our work will offer some efforts for the preparation of functional materials with excellent properties.

Introduction

Al$_2$O$_3$ aerogels are attractive materials due to their fascinating chemical and textural properties, such as large specific areas, high porosity, and low density/thermal conductivity, which makes them interesting for a wide variety of fields ranging from thermal insulation, catalyst supports, biomaterials, and energy storage and conversion [1, 2]. A variety of Al$_2$O$_3$ aerogels have been synthesized by different kind of preparation methods, including sol-gel, liquid exfoliation, and chemical vapor deposition [3–5]. These prepared aerogel materials have good adsorption properties [5–8], thermal stability [9], catalytic activity [10–13], and high-temperature resistance [14]. Currently, most efforts have been made to improve the physical and chemical properties of Al$_2$O$_3$ aerogel materials by introducing other chemical materials such as chitosan [5, 9], montmorillonite and carbon nanotube [15], SiO$_2$ [9], CaO [16, 17], ZrO$_2$ [18–20] into Al$_2$O$_3$ aerogels and develop simple and convenient drying techniques to reduce the cost of preparation. Meanwhile, ambient pressure drying technology is an important research aspect on Al$_2$O$_3$ aerogel material. Since the conventional drying techniques are relatively costly, risky, and time-consuming, which severely limits their large-scale practical applications [9]. In fact, the properties of Al$_2$O$_3$ aerogel materials are greatly affected by the microstructure after introducing different substances. However, only a few literatures reported on the microstructure influence on Al$_2$O$_3$ aerogel materials after adding different substances. Hence, in this work, we design to synthesize a series of metal composite Al$_2$O$_3$ aerogel materials by doping different transition metals/lanthanides ions in Al$_2$O$_3$ aerogel matrix (Ni$^{2+}$, Co$^{2+}$, Eu$^{3+}$, Tb$^{3+}$, Ce$^{3+}$). The microstructure change of those metal composite Al$_2$O$_3$ aerogel materials were investigated and comparison. Through this work, we could have a relatively comprehensive understanding of the influence of different transition metals/lanthanides ions on the microstructure of metal...
composite Al$_2$O$_3$ aerogel materials, which play a positive role in improving Al$_2$O$_3$ aerogel and other composite materials.

Luminescent materials have attracted much attention in many fields as lighting, display, information, medicine, military due to their outstanding advantages of high color purity, bright colors, good conversion efficiency, stable properties, and many types of emitting spectra [21–25]. With the improvement of social development requirements and the progress of lighting industry technology, a variety of rare earth luminescent materials have been prepared by different methods such as sol-gel method, chemical vapor deposition, precipitation, and high temperature solid phase synthesis [26]. Based on the consistency of photovoltaic technical indicators and products, reducing consumption, optimizing utilization, and further improving luminescence efficiency are the important ways to protect rare earth resources. Over the past years, increasing efforts have been devoted to the design and developing of luminescent materials with multifunctional properties. However, only a few literatures reported on the microstructure influence on luminescent materials by doping or co-doping Eu$^{3+}$, Tb$^{3+}$ and Ce$^{3+}$ ions. Moreover, very few researchers have made systematical research on the change in microstructure to the influence of doping transition metals/lanthanides metal ions. The luminescent materials consist of lanthanides metal ions and matrix [27]. Eu$^{3+}$, Tb$^{3+}$ and Ce$^{3+}$ are commonly used as efficient luminescent centers in display application [28]. The current research on improving luminescence properties is mainly focused on adjusting doping types of lanthanides metal ions, increasing doping concentration, and changing the substrate type, etc [29–33]. However, the substrate bears the responsibility to load, disperse and provide crystal fields and emission sites for excited lanthanides metal ions, which directly affects the luminescence efficiency and final properties of luminescent material [34]. Thus, it has been an attractive research field that design the structural of substrate for the synthesis of luminescent materials [35]. The first step is to select matrix with good properties. Among the existing substrates, oxide matrix had the advantages of simple preparation process and stable performance. It includes non–rare earth oxide substrates (such as TiO$_2$, ZnO, ZrO$_2$, Al$_2$O$_3$) and rare earth oxide substrates (Y$_2$O$_3$, Gd$_2$O$_3$, Lu$_2$O$_3$) [36–38].

Al$_2$O$_3$ is considered as a good matrix since it has many excellent properties such as lower phonon energy, wider band gap (about 8.7 eV), high mechanical strength and good physical and chemical and thermal stability. It also has the same or similar metal valence and crystal structure as rare earth oxides and is suitable for the loading dispersion and high concentration doping of lanthanides metal ions [39]. Although Al$_2$O$_3$ had good properties, while used as matrix to disperse lanthanides metal ions, the active luminescent sites on the surface of Al$_2$O$_3$ powder matrix limit the improvement of luminescence properties due to its lower specific surface area. The effects of high temperature on the microstructure, pore size and nano particle size of matrix also limits the improvement of luminescence properties. After calcination at high temperature, the structural stability still needs to be improved. Since the lanthanides metal ions are passively loaded on the substrate, which can emit light on the surface of substrate. While the lanthanides metal ions were wrapped or covered in the inner layer or combined weakly with the substrate, agglomeration and shedding occurred during high temperature calcination, which limited the further improvement of luminescence properties. This problem also exists in catalyst and is one of the main reasons that affect the enhancement of catalytic activity. Aerogels are unique three-dimensional porous structure materials with high surface areas, large open pores, and good chemical thermal stability, which have been widely used in many fields, such as high temperature insulation, special electrode materials, and catalyst carrier, etc [40–42]. Al$_2$O$_3$ aerogel is a well-known substrate material for lanthanides metal ions and has been widely used in various fields [43–45]. However, researchers focus most interests on studying the effect of lanthanides metal ions concentration and the type of different matrix for luminescence properties in recent years [46, 47]. Hence, there is still much room for developing simple and fast method for the synthesis of a range of three-dimensional nano porous aerogel luminescence materials with high surface area, well controlled morphology, surface conditions and size.

Herein, we design to synthesize a serious of three-dimensional nano porous Ni$^{2+}$, Co$^{2+}$, Eu$^{3+}$, Tb$^{3+}$, and Ce$^{3+}$ doped or co-doped Al$_2$O$_3$ aerogel materials by a modified, simple, and facile sol–gel method. The microstructure of these aerogel materials was investigated. The effect of different transitions/lanthanides metal ions on the microstructure, textural properties, and luminescence properties on the of Al$_2$O$_3$ aerogel materials were also investigated. Moreover, by doping or co-doping the Al$_2$O$_3$ aerogel matrix with Eu$^{3+}$ and Tb$^{3+}$, we managed to synthesize luminescent materials with tunable color emissions. The luminescence properties of as-prepared Al$_2$O$_3$ aerogel luminescent materials were analyzed. The effect of different calcination temperatures on luminescence properties of Al$_2$O$_3$ aerogel luminescent materials was studied and discussed. We expect that our work could provide an alternative guide to fabricating aerogel or other functional materials with excellent properties.
**Table 1.** Chemical composition of prepared metal Al2O3 composite aerogel materials.

| Sample       | Chemical composition                                                                 | Molar ratios   |
|--------------|---------------------------------------------------------------------------------------|----------------|
| Al2O3-Ni (II)| NiCl3·6H2O: Al2O3·6H2O: H2O: C6H5OH: PO                                             | 1:1:5:2:10:10  |
| Al2O3-Co (II)| CoCl3·6H2O: Al2O3·6H2O: H2O: C6H5OH: PO                                             | 1:1:5:2:10:10  |
| Al2O3-Eu (III)| EuCl3· AlCl3·6H2O· H2O: C6H5OH: PO                                                  | 1:20: 300:400:200 |
| Al2O3-Tb (III)| TbCl3· AlCl3·6H2O· H2O: C6H5OH: PO                                                | 1:20: 300:400:200 |
| Al2O3-Ce (III)| CeCl3· AlCl3·6H2O· H2O: C6H5OH: PO                                               | 1:20: 300:400:200 |
| Al2O3-Eu/Tb (III)| TbCl3· EuCl3· AlCl3·6H2O· H2O: C6H5OH: PO                          | 1:2:70: 900:1300:700 |
| Al2O3-Eu/Ce (III)| CeCl3· EuCl3· AlCl3·6H2O· H2O: C6H5OH: PO                                | 1:2:70: 900:1300:700 |
| Al2O3-Tb/Ce (III)| CeCl3· TbCl3· AlCl3·6H2O· H2O: C6H5OH: PO                                | 1:2:70: 900:1300:700 |

**Experimental details**

**Materials**

AlCl3·6H2O (97.2%), NiCl2·6H2O (99.8%), CoCl2·6H2O (99.8%), EuCl3 (99.9%), TbCl3 (99.8%), CeCl3 (99.8%), anhydrous ethanol (99%), 1, 2-epoxy propane (PO, 98.8%) were supplied by Shanghai Aladdin Chemical Co., Ltd, China. All materials were used without further purification, and all solutions were prepared with deionized water.

**Synthesis of Ni2+, Co2+, Eu3+, Tb3+, Ce3+-doped or co-doped Al2O3 aerogel materials**

The detailed preparation process of these Ni2+, Co2+, Eu3+, Tb3+, Ce3+-doped or co-doped Al2O3 aerogel materials are similar to our previous reported literature [1,2]. In a typical process, the Al2O3 sol was synthesized by hydrolysis and polycondensation AlCl3·6H2O at 100 °C with a molar ratio of AlCl3·6H2O: NiCl3·6H2O: C6H5OH: H2O: PO of 1: 1.5: 2: 10: 10. After cooling to room temperature, 32 ml of 1, 2-epoxy propane was added into the Al2O3 sol dropwise and kept stirring for 35 min to obtain gel. The resulting solution was poured into glass bottles and washed at least three times using distilled water. After that, 40 ml of C6H5OH was added to age for 48 h, and the absolute ethyl alcohol should be changed for two times during the process to fill the pores with alcohol. The Al2O3-Ni (II) aerogel was obtained by drying in a vacuum oven for 5 h and then calcinated at 550, 650 and 750 °C in a muffle furnace with a heating rate of 5 °C min⁻¹. Al2O3-Co (II), Al2O3-Eu (III), Al2O3-Tb (III), and Al2O3-Ce (III) aerogel materials were prepared by the same preparation process, and their chemical compositions and molar ratios were shown in table 1. Eu3+, Tb3+, Ce3+ co-doped Al2O3 aerogel materials were synthesized by using the similar steps as Al2O3-Ni (II) aerogel material. However, the first step is changed to the exact amount of AlCl3·6H2O, EuCl3 and TbCl3 were dissolved into 27 ml of absolute ethanol and 12 ml of deionized water mixed solution with stirring for 15 min. All other steps were the same as for the synthesis of Al2O3-Eu/Tb (III), Al2O3-Eu/Ce (III) and Al2O3-Tb/Ce (III) luminescent aerogel materials.

**Characterization**

X-ray powder diffraction (XRD) patterns were analyzed on an Ultima IV x-ray diffractometer (Rigaku, Tokyo, Japan) and equipped with Cu Kα radiation (45 kV, 40 mA) to investigate the crystal structure of the prepared metal Al2O3 composite aerogel materials. The scanning electron microscope (SEM) images were performed on a JEOI JSM-5600L instrument to obtain the microstructure of metal Al2O3 composite aerogel materials. Transmission electron microscopy (TEM) images were analyzed on a JEM-2011 microscope at 200 kV to study the dispersion of metal nanoparticles on Al2O3 aerogel matrix. N2 adsorption-desorption analysis was examined by using an ASAP2020 surface area analyzer at 77 K to evaluate the surface area and pore size distribution of metal Al2O3 composite aerogel. Prior measurement, these aerogel materials were outgassed in vacuum at 120 °C for 12 h. Surface area was calculated based on the BET model, and pore size distribution and total pore volume were evaluated using BJH method. JASCO FP-8500 luminescence spectrometer was used to recorded the excitation and emission spectra of the metal Al2O3 composite aerogel materials.

**Results and discussion**

**Effect of different transitions/lanthanides metal ions on the microstructure of Al2O3 aerogel materials**

As illustrated in figure 1(a), the entire fabricated process of the metal Al2O3 composite aerogel materials consisted of gelation, vacuum drying, and calcination. Take the synthesis of Al2O3-Ni (II) aerogel as an example, the sol was prepared by stirring a mixture of precursor AlCl3·6H2O, NiCl2·6H2O, and C6H5OH chemicals. The sol was sealed and heated at 100 °C for 1 h to form gel solution through hydrolysis and condensation polymerization. The gel solution was dried via vacuum drying process and then calcined in air at different
temperature (550 °C–750 °C) for 2.5 h to obtain Al2O3-Ni (II) aerogel. The same fabricated process can also be applied to other metal Al2O3 composite aerogels. Characterizations of the structural and physical properties of these prepared metal Al2O3 composite aerogels were conducted. Prior to each test, all aerogel samples were calcinated at different high-temperature for 2.5 h to completely remove the residual water and solvent in the channel. The aerogel samples calcinated at 650 °C were chosen for characterization tests. Figures 1(b)–(h) presents the SEM images of Al2O3-Ni (II), Al2O3-Co (II), Al2O3-Ce (III), Al2O3-Eu/Ce (III), Al2O3-Eu/Tb (III), Al2O3-Tb/Ce (III), and Al2O3-Tb (III) aerogel materials. From the SEM images of these aerogel materials, we can observe that the microstructure of transition metal composite Al2O3 aerogels (Al2O3-Ni (II) and Al2O3-Co (II)) and lanthanides metal ions composite Al2O3 aerogels (Al2O3-Ce (III), Al2O3-Eu/Ce (III), Al2O3-Eu/Tb (III), Al2O3-Tb/Ce (III), and Al2O3-Tb (III)) are significantly different.

The three-dimensional nano porous structure of Al2O3-Ni (II) and Al2O3-Co (II) aerogels were composed of a large number of colloidal particles with relatively small size. Many pores with different pore diameters were distributed among these colloidal particles [48] (figures 1(b) and (c)). Interestingly, by doping or co-doping the same Al2O3 aerogel matrix with Eu3+, Tb3+, and Ce3+, we found that the microstructure of these lanthanides metal ions composite Al2O3 aerogels were also different. Figure 1(d) presented the SEM image of Al2O3-Ce (III) aerogel material, it can be clearly observed that Al2O3-Ce (III) was a three-dimensional porous structure composed of irregular block. The irregular block was composed of several flakes, and the flakes were closely connected to each other and a great number of the pores were present in irregular blocks (figures S1(a)–(d) (available online at stacks.iop.org/NANOX/2/030006/mmedia)). The microstructure of the Al2O3-Eu/Ce (III) aerogel material are displayed in figures 1(e) and S2(a)–(d). Compare to the Al2O3-Ce (III), the Al2O3-Eu/Ce (III) aerogel had a uniform porous structure composed of several spherical nanoparticles, and almost no holes
can be clearly observed on the surface of spherical nanoparticles. Figures 1(f) and S3(a)–(c) showed the SEM images of the Al₂O₃-Eu/Tb (III) aerogel luminescent material after annealing in air at 750 °C for 2.5 h, and the material emitted light red under excitation of 254 nm ultraviolet light (shown below). The low magnification SEM images showed that the morphology of the material was many spherical particles adhered to each other and clustered together. The microstructure of sample resembled a special flower-like with further enlarged particles. The surface was enriched with countless small holes, and when the surface microstructure was further enlarged, it can be seen that it was composed of numerous lamellar or lamellar structures. There were numerous pores between the lamellar structures, and the size of each pore was different, which also indicated that the as-prepared materials were three-dimensional nano porous structure. The adhesion between the sheets was not very close, dense and relatively uniform, suggesting that the introduction of Eu³⁺ and Tb³⁺ ions can be better combined and dispersed in the Al₂O₃ aerogel matrix. Even after 750 °C high temperature calcination, the microstructure of the material still did not occur serious agglomeration or aggregation, which helped to retain the luminescence site of the Al₂O₃-Eu/Tb (III) aerogel luminescent materials, thus improving the luminescence properties of material. Moreover, these results showed that the lanthanides metal ions were dispersed and combined well with the Al₂O₃ aerogel matrix, and the addition of Eu³⁺ and Tb³⁺ co-doped had a great influence on the microstructure of Al₂O₃ aerogel matrix. The lanthanides metal ions also had a strong binding force with the Al₂O₃ aerogel matrix, which was conducive to effectively improve the luminescent properties of materials. Since the luminescent sites of lanthanides metal ions could still be attached to the Al₂O₃ aerogel substrate without falling off or producing severe agglomeration when the sample subjected to high temperature calcination, which seriously affected the luminescence properties of the materials. The microstructure of Al₂O₃-Tb/Ce (III) aerogel material was similar to Al₂O₃-Eu/Tb (III), according to figures 1(g) and S4(a)–(d). It is demonstrated that many flakes formed in the flower-like spherical particles, and they stayed in an interlocking state and connected relatively compactly to construct the three-dimensional porous structure. In comparison, we speculate that the Tb³⁺ ion can regulate the microscopic growth morphology of Al₂O₃-Tb/Ce (III) and Al₂O₃-Eu/Tb (III) aerogel materials to form a three-dimensional porous structure composed of several special flower-like spherical nanoparticles.

The SEM images of Al₂O₃-Tb (III) aerogel luminescent material was shown in figure 1(h). The microscopic morphology of the sample was composed of spherical particles with different sizes and irregular blocks upon doping with Tb³⁺ (figures S5(a)–(d)). When one of the spherical particles was enlarged, it can be found that some spherical particles and irregular blocks were attached to its surface. Moreover, there were not many holes existed, and the surfaces were relatively compact, which was obviously different from the microscopic morphology of the material by co-doping Eu³⁺ and Tb³⁺, indicating that the introduction of different lanthanides metal ions had a great influence on the microscopic morphology of the three-dimensional nano porous Al₂O₃ aerogel-based luminescence materials, which could be attributed to the properties of lanthanides metal ions and the different binding reaction with Al₂O₃ aerogel matrix. These results indicated that a different small amount of lanthanides metal ions could be regulated the microstructure and structure of Al₂O₃ aerogel matrix obviously.

The microstructure of all metal Al₂O₃ composite aerogel materials were also analyzed by TEM and HRTEM analysis, according to figure 2(a)–(t). The original Al₂O₃ aerogel matrix showed many lamellar structures (figure 2(a)). While different transitions/lanthanides metal ions were introduced, the microstructure of Al₂O₃ aerogel matrix began to change. It can be clearly observed that the Ni and Co nanoparticles were anchored and well distributed inside the Al₂O₃ aerogel matrix (figures 2(b)–(g)). Many lamellar structures of the original Al₂O₃ aerogel matrix disappeared, and different morphologies appeared with different transition metal ions doping, indicating that the properties of Ni²⁺ and Co²⁺ had an impact influence on the same Al₂O₃ aerogel matrix. These two transition metal ions have the same valence state, the further research can continue in-depth study of the following aspects: to follow what the specific factor that cause the change of microstructure of Al₂O₃ aerogel matrix. The conclusions in this paper will be of some value for the later reference, such as the studying methods, the data, and the changing tendency of performance parameters. Both the outline of Ni, Co nanoparticles and Al₂O₃ aerogel matrix could be observed obviously, and Ni nanoparticles are much smaller and have more numerous compared to Co nanoparticles. Moreover, there was no aggregation among the Ni and Co nanoparticles.

Figures 2(h) and (i) present the TEM images of Al₂O₃-Eu (III) aerogel, and we found that the nano particles can be observed in the sample, suggesting that the Eu³⁺ ions may have well dispersed in Al₂O₃ aerogel matrix. The sample had a texture structure composed of flocculent or filamentous, and they were related to each other to some extent. Meanwhile, Al₂O₃-Ce (III) aerogel material are different from the Al₂O₃-Eu (III), which some small nano particles can be observed in the texture structure composed of thin flakes (figures 2(j) and (k)). Compared to Al₂O₃-Eu (III) and Al₂O₃-Ce (III) aerogel materials, by co-doping the Al₂O₃ aerogel matrix with Ce³⁺ and Eu³⁺ ions, we found that the Al₂O₃-Eu/Ce (III) consisted of thin flakes and flocculent intertwined (figures 2(i) and (m)). Figures 2(n) and (o) showed the TEM images of the Al₂O₃-Eu/Tb (III) aerogel
luminescent material after annealing in air at 750 °C for 2.5 h. Unlike transition metals, any lanthanides metal nanoparticles can be observed in the Al₂O₃ aerogel matrix. The microscopic structure of luminescent material was spherical nanoparticles, and the two nanoparticles were connected, which may be due to van der Waals force or electrostatic attraction. After magnification, the lanthanides metal nanoparticles were relatively uniformly dispersed on the Al₂O₃ aerogel matrix without obvious agglomeration or aggregation. The matrix presented a flake or tulle-like shape. The rod shape appearing in figure 2(o) may be due to the flake shape of Al₂O₃ aerogel matrix had been folded. Meanwhile, the unfolded parts were still showed a tulle shape. The TEM images of Al₂O₃-Ce/Tb (III) aerogel material were shown in figures 2(p) and (q), which were similar to Al₂O₃-Eu/Tb (III) aerogel. In contrast, the microscopic morphology of the nanoparticles of Al₂O₃-Tb (III) aerogel luminescent material was not spherical, however, irregular block, and the lanthanides metal nanoparticles had a certain agglomeration, according to figures 2(r)–(t). The overall particle sizes were relatively large, indicating that its dispersion on the Al₂O₃ aerogel matrix needed to be improved, and the morphology of different blocks were also different. At the same time, the morphology of the Al₂O₃ aerogel matrix also changed greatly, since it was no
longer lamellar or thin layered, implying that the addition of different lanthanides metal ions had great influence on the microstructure morphology of the same matrix.

Effect of different transitions/lanthanides metal ions on the textural properties of Al₂O₃ aerogel materials

XRD analysis

Characterizations of the structural and physical properties of these metal Al₂O₃ composite aerogel materials before and after calcination were performed. The x-ray diffraction (XRD) patterns of these samples were shown in figures 3(a)–(e). The diffraction peaks of Al₂O₃ aerogel matrix, Al₂O₃-Ni(II), and Al₂O₃-Co(II) were coincident with Al₂O₃ (JCPDS 47-1292), NiO (JCPDS 04-0835), and cubic phase CoO (JCPDS 43-1003), and no new diffraction peaks were observed. Compared to lanthanides metal ions composite Al₂O₃ aerogel materials, Al₂O₃-Ni(II) and Al₂O₃-Co(II) aerogels displayed stronger diffraction peaks, indicating that the transition metal composite Al₂O₃ aerogels had better crystallinity after calcination. The Al₂O₃-Ce(III) showed the best strong diffraction peaks in lanthanides metal ions composite Al₂O₃ aerogel materials after calcination, and the reflections in the patterns had shifted or disappeared with the increasing of calcination temperature. For instance, the diffraction peaks of Al₂O₃ aerogel appeared at around 40° and 60° [38], however, after the introduction of Eu³⁺ and Tb³⁺, these two diffraction peaks were basically invisible, indicating that the addition of Eu³⁺ and Tb³⁺ had an effect on the structural properties of Al₂O₃-Eu/Tb(III) aerogel luminescent material. The crystallinity, degree of order, strength and symmetry of Al₂O₃ aerogel matrix were reduced. These changes were good for the luminescence of co-doped Eu³⁺ and Tb³⁺. The as-prepared samples before and after calcination at different temperature showed the characteristic diffraction peaks at 10° and 21°, which could be attributed to the diffraction of EuO₄ and Tb₂O₇ [38, 46, 48]. With an increase of the annealing temperature, the peak intensity did not become sharp, and even raising the calcination temperature to 750 °C, it still did not change. In addition, when the calcination temperature was 550 and 650 °C, the positions of the two peaks were shifted and the intensity was decreased, indicating that increasing the calcination temperature had limited influence on the crystallinity of Al₂O₃-Eu/Tb(III) and Al₂O₃-Tb(III) aerogel luminescent materials. This phenomenon is different from what has been reported in other literature [22, 26]. The results suggested that expect for Al₂O₃-Ce(III), the other lanthanides metal ions composite Al₂O₃ aerogel materials prepared by sol-gel method were amorphous.

BET analysis

To investigate the Brunauer–Emmett–Teller (BET) surface area, pore size distribution and porosity of these metal Al₂O₃ composite aerogel materials, nitrogen adsorption analysis was conducted (figures 4(a)–(e)). Based on the IUPAC classification, the isotherms of all samples feature type IV curves, and had a H1 hysteresis loops, which were the basic characteristic of 1D cylindrical pore structure material (figures 4(a)–(e)). Except for

Figure 3. XRD patterns of the (a) Al₂O₃-Ce(III), Al₂O₃-Eu/Ce(III), Al₂O₃-Eu/Tb(III), Al₂O₃-Ce/Tb(III), and Al₂O₃-Tb(III) aerogel luminescent materials annealed at different temperatures (550, 650 and 750 °C), respectively.
Al₂O₃-Tb (III), the isotherms of the other Al₂O₃ aerogel materials were similar, even after annealing in air at 750 °C for 2.5 h. The BET surface area and pore size distribution curves (inset) of all samples before and after calcination were determined and summarized in tables 2 and 3. It can be deduced that, before calcination, these metal Al₂O₃ composite aerogel materials had similar BET surface area in the region of 262.9 ~ 339.6 m²·g⁻¹, the pores were relatively smaller and pore sizes were mainly concentrated in the region from 5 to 25 nm. After annealing, the specific surface area of these aerogel materials had decreased to 177.9 ~ 244.1 m²·g⁻¹, which showed good agreement with other literature reported [9, 16]. Moreover, the pore sizes tended to increase, and the degree of increase was not very large, indicating that the materials could maintain the integrity and stability of the three-dimensional nano porous structure after being subjected to high temperature treatment. These results indicated that the specific surface area and pore sizes of most Al₂O₃ composite aerogel materials prepared by sol-gel method were in the similar interval, implying that it had to do more with the nature of the aerogel materials than the types of material introduced.

Figure 4. Complete adsorption−desorption isotherms and BET surface area and pore size distribution (inset) of the (a) Al₂O₃-Ce (III), (b) Al₂O₃-Eu/Ce (III), (c) Al₂O₃-Eu/Tb (III), (d) Al₂O₃-Tb/Ce (III), and (e) Al₂O₃-Tb (III) aerogel materials before (red line) and after (black line) annealing in air at 750 °C for 2.5 h.
Effect of different lanthanides metal ions on the luminescence properties of Al₂O₃ aerogel materials

Luminous color

The luminescent aerogel materials with tunable color have attracted wide attention due to its important application in photoelectric devices and various fields [47, 48]. Al₂O₃-Eu/Tb (III) and Al₂O₃-Tb (III) aerogel luminescent materials were selected for studying the effect of different lanthanides metal ions on the luminescence properties of Al₂O₃ aerogel materials. Figure 5 showed the tunable colors of the Al₂O₃-Eu/Tb (III) and Al₂O₃-Tb (III) aerogel luminescent materials excited by 254 and 365 nm ultraviolet light, respectively. The digital photographs (No. 1–8) showed the red light of Al₂O₃-Eu/Tb (III) aerogel luminescent material that excited by 254 and 365 nm ultraviolet light, respectively. After calcination at 550 °C, whether it was excited at 254 or 365 nm, the material all emitted red light. Moreover, after enhancing the calcination temperature to 650 and 750 °C, the material emitted red light under excitation of 254 nm ultraviolet light, and still emitted red light under excitation of 365 nm ultraviolet light. It was worth mentioning that the brightness of the light was not reduced. Combined with SEM and BET characterization, it was indicated that the specific surface area of material decreased and the pore structure collapsed to a certain extent after undergoing high-temperature calcination, and the overall structure remained relatively intact. For Al₂O₃-Tb (III) aerogel luminescent material, it emitted special light under excitation of 254 nm and 365 nm excitation as shown in digital photographs (No. 9–16). After calcination at different temperatures (550 °C–750 °C), the sample emitted green light, and the color did not decrease with the increase of calcination temperature, implying that the luminescence properties of the Al₂O₃-Eu/Tb (III) and Al₂O₃-Tb (III) aerogel luminescent materials was relatively stable.

Photoluminescence properties

Figure 6(a) showed the excitation spectra of Al₂O₃-Eu/Tb (III) and Al₂O₃-Tb (III) aerogel luminescent materials at the monitoring wavelengths of 613 and 544 nm, respectively. The Al₂O₃-Tb (III) aerogel sample appeared three excitation peaks at 284, 350 and 380 nm, which were attributed to the 5D₄ → 7F₆, 5D₄ → 7F₅, and 7F₆ → 5G₄ transition of Tb³⁺ ions. The strongest excitation peak appeared at 284 nm. Eu³⁺ had a relatively weak broadened absorption peak at 265 nm, which could be attributed to the excitation peak of Tb³⁺ at 284 nm overlapped with the excitation peak of Eu³⁺ at 265 nm. Meanwhile, Tb³⁺ and Eu³⁺ meet the principle of radiant energy transfer. While Tb³⁺ and Eu³⁺ absorbed the excitation energy, Tb³⁺ transferred non-radiative energy to Eu³⁺, resulting in a significant increase in the excitation peak of Al₂O₃-Eu/Tb (III) samples at 265 nm wavelength. Figures 6(b) and (c) showed the emission spectra of Al₂O₃-Eu/Tb (III) and Al₂O₃-Tb (III) aerogel luminescent materials after annealing at 550 and 750 °C under different excitation peaks. It can be clearly observed that four strong peaks appeared at the Al₂O₃-Tb (III) aerogel sample at the excitation wavelength of 284 nm after annealing at 550 °C. These four peaks were located at 490, 544, 585 and 615 nm, which can be attributed to the Tb³⁺ transitions of 5D₄ → 7F₆, 5D₄ → 7F₅, 5D₄ → 7F₄ and 5D₄ → 7F₃, respectively. Among these, the light emitted by the 5D₄ → 7F₄ transition at 544 nm in the green region was the strongest. The

### Table 2. Textural properties of prepared aerogels before calcination.

| Sample          | Sₜot (m² g⁻¹) | Average pore diameter (nm) | Pore volume (cm³ g⁻¹) |
|-----------------|--------------|---------------------------|----------------------|
| Al₂O₃-Ni (II)   | 325.0        | —                         | —                    |
| Al₂O₃-Co (II)   | 268.5        | —                         | —                    |
| Al₂O₃-Ce (III)  | 321.2        | 8.79                      | 0.78                 |
| Al₂O₃-Eu/Co (II)| 339.6        | 9.16                      | 0.87                 |
| Al₂O₃-Eu/Tb (III)| 262.9       | 12.88                     | 0.79                 |
| Al₂O₃-Ce/Tb (III)| 304.8       | 10.56                     | 0.85                 |
| Al₂O₃-Tb (III)  | 318.9        | 8.72                      | 0.75                 |

### Table 3. Textural properties of prepared aerogels after calcination.

| Sample          | Sₜot (m² g⁻¹) | Average pore diameter (nm) | Pore volume (cm³ g⁻¹) |
|-----------------|--------------|---------------------------|----------------------|
| Al₂O₃-Ni (II)   | 191.2        | —                         | —                    |
| Al₂O₃-Co (II)   | 177.0        | —                         | —                    |
| Al₂O₃-Ce (III)  | 244.1        | 29.89                     | 1.71                 |
| Al₂O₃-Eu/Co (II)| 209.3        | 30.2                      | 1.45                 |
| Al₂O₃-Eu/Tb (III)| 186.1       | 21.5                      | 1.06                 |
| Al₂O₃-Ce/Tb (III)| 218.3       | 20.18                     | 1.05                 |
| Al₂O₃-Tb (III)  | 177.9        | 14.9                      | 0.68                 |
Al₂O₃-Eu/Tb (III) sample had the strongest luminescence intensity at the excitation wavelength of 265 nm after annealing at 750 °C. Similarly, the sample showed three strong peaks at the excitation wavelength of 265 nm after annealing at 750 °C, which were located at 590, 613 and 695 nm, respectively, corresponding to the ⁵D₀ → ⁷F₅, ⁵D₀ → ⁷F₂, and ⁵D₀ → ⁷F₃ transitions [49]. Compared to the magnetic dipole transition of ⁵D₀ → ⁷F₁ at 590 nm, the electric dipole transition of ⁵D₀ → ⁷F₂ at 613 nm was much stronger, which was generally considered that Eu³⁺ was located near the non-uniform lattice field on the surface of the Al₂O₃ substrate, leading to an increase in the probability of ⁵D₀ → ⁷F₂ energy level transition and enhanced luminescence properties. Another explanation was that as the annealing temperature increased, the coordination configuration of the sample changed from cubic phase structure to monoclinic phase structure, thereby enhancing the energy level splitting of lanthanides ions. The emission peak at 590 nm showed a multiple, and the emission peak at 613 nm had a shoulder peak. In addition, when the calcination temperature increased from 550 to 750 °C, the intensity of the emission peak and the excitation peak was significantly enhanced, suggesting that the Al₂O₃ aerogel luminescent materials could maintain good luminescence intensity and luminescence sites after being subjected to high temperature treatment, which promoted the improvement of the luminescence intensity of the Al₂O₃ aerogel luminescent materials.

Conclusions

We presented in this work a simple, facile yet effective method to synthesize three-dimensional nano porous different transitions/lanthanides metal ions Al₂O₃ aerogel materials. The effect of different transitions/
Lanthanides metal ions on the microstructure, textural properties, and luminescence properties of Al₂O₃ aerogel materials were discussed in detail. It is expected that this work will provide some small part in helping future developments in fabricating functional aerogel materials or other materials with excellent properties for various applications. Furthermore, by co-doping the Al₂O₃ aerogel matrix with Eu³⁺ and Tb³⁺, we successfully prepared luminescent aerogel materials with tunable color emissions under UV illumination. An improved of calcination temperature from 550 to 650 °C induced a remarkably tunable emission. The luminescent aerogel materials with green color emissions under UV illumination can be prepared by doping the Al₂O₃ aerogel matrix with Tb³⁺. The SEM images showed that the morphology of Eu³⁺ and Tb³⁺ co-doped Al₂O₃ aerogel luminescent material was flower-like, and the morphology changed greatly by doping the Al₂O₃ aerogel matrix with single Tb³⁺ ions. Moreover, the results showed that the three-dimensional nano porous structure of Al₂O₃ aerogel luminescence materials remained relatively intact after 750 °C high temperature treatment, indicating that luminescence sites of rare earth metal ions did not decrease dramatically. The Eu³⁺ and Tb³⁺ could be strongly assembled into the three-dimensional network framework of Al₂O₃ aerogel matrix by hydrolysis and condensation polymerization reactions during the preparation process, which helps to solve the problem of agglomeration or shedding caused by the passive loading of rare earth metal ions on the substrate. After the high temperature treatment at 750 °C, the PL peak intensity of the Al₂O₃ aerogel luminescent materials was significantly increased, indicating that not only the crystallinity of the material was improved, but also the luminescence properties were improved. We expect that this study could provide an alternative approach for the preparation of three-dimensional nano porous Al₂O₃ aerogel luminescence materials with high luminescence performance.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Declarations

Conflict of interest

The authors declare no competing financial interest. The first two authors contributed equally to this work and can be considered co-first authors.

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References

[1] Feng J et al 2021 Printed aerogels: chemistry, processing, and applications Chem. Soc. Rev. 50 3842–88
[2] Maleki H, Durves L, Garcia-Gonzalez C A, Del Gaudio P, Portugal A and Mahmoudi M 2016 Synthesis and biomedical applications of aerogel capacities and challenges Adv. Colloid Interface Sci. 236 27
[3] Ravishankar K, Shelly K, Desingh P, Subramaniam R, Narayanan A and Dhamodharan R 2018 Green, solid-state synthesis of maleated chitosan and ionotropic gelation with chitosan ACS Sustain. Chem. Eng. 6 15191
[4] Ren W et al 2018 Recyclable metal-organic framework/cellulose aerogels for activating peroxymonosulfate to degrade organic pollutants Chem. Eng. J. 349 706
[5] Liao J, Zhang Y and Zhang L 2020 Improved catalytic activity on the thermal decomposition of ammonium perchlorate and efficient adsorption of uranium using a novel ultra-low density Al2O3-based aerogel J. Hazard. Mater. 387 122015
[6] Cao Q, Huang F, Zhuang Z and Lin Z 2012 A study of the potential application of nano Mg(OH)2 in adsorbing low concentrations of uranyl tricarboxate from water. Nanoscale 4 2423
[7] Li B et al 2017 Functionalized porous aromatic framework for efficient uranium adsorption from aqueous solutions. ACS Appl. Mater. Interfaces 9 12511
[8] Huang S et al 2018 Unexpected ultrafast and high adsorption of U(VI) and Eu (III) from solution using porous Al2O3 microspheres derived from MIL-53 Chem. Eng. J. 353 157
[9] Yang Z, Zhu D and Li H 2019 A chitosan-assisted co-assembly synthetic route to low-shrinkage Al2O3–SiO2 aerogel via ambient pressure drying Micropor. Mesopor. Mat. 293 109781
[10] Umdu E S, Tuncer M and Seker E 2009 Transesterification of nannochloropsis oculata microalgae’s lipid to biodiesel on Al2O3 supported CaO and MgO catalysts Bioresour. Technol. 100 2828
[11] Umdu E S and Seker E 2012 Transesterification of sunflower oil on single step sol-gel made Al2O3 supported CaO catalysts: effect of basic strength and basicity on turnover frequency Bioresour. Technol. 106 178
[12] Gao B, Wang I-W, Ren L, Haines T and Hu J 2019 Catalytic performance and reproducibility of Ni/Al2O3 and Co/Al2O3 mesoporous aerogel catalysts for methane decomposition Ind. Eng. Chem. Res. 58 7958
[13] Gao B, Wang I-W, Ren L and Hu J 2019 Catalytic methane decomposition over bimetallic transition metal supported on composite aerogel Energy & Fuels 33 9099
[14] Zhang X et al 2020 Ultrastrong, superelastic, and lamellar multiarch structured ZrO2–Al2O3 nanofibrous aerogels with high-temperature resistance over 1300 °C ACS Nano 14 15616
[15] Chen J, Xie H, Lai X, Li H, Gao J and Zeng X 2020 An ultrasensitive fire-warning chitosan/montmorillonite/carbon nanotube composite aerogel with high fire-resistance Chem. Eng. J. 399 125729
[16] Kesserwan F, Mohammad N A, Khalil M and Houssam E R 2020 Hybrid CaO/Al2O3 aerogel as heterogeneous catalyst for biodiesel production Chem. Eng. J. 385 125438
[17] Witoon T, Bumrungsalee S, Vathavanichkul P, Palitsakan S, Saisiriyoot M and Faungnawakij K 2014 Biodiesel production from transesterification of palm oil with methanol over CaO supported on bimodal meso-macroporous silica catalyst. Bioresour. Technol. 156 329
[18] Wu X, Shao G, Shen X, Cui S, Wang L and Shen X 2016 Synthesis of a novel Al2O3–SiO2 composite aerogel with high specific surface area at elevated temperatures using inexpensive inorganic salt of aluminum Ceram. Int. 42 874
[19] Wu X, Shao G, Shen X, Cui S and Wang L 2016 Novel Al2O3–SiO2 composite aerogels with high specific surface area at elevated temperatures with different alumina/silica molar ratios prepared by a non-alkoxide sol–gel method RSC Adv. 6 56311
[20] Feng F, Jiang Y, Feng J, Li L, Cai H and Feng J 2020 A facile method to fabricate monolithic alumina–silica aerogels with high surface areas and good mechanical properties J. Eur. Ceram. Soc. 40 2480
[21] Jankowski R and Sieklucka B 2019 Near-infrared emissive Er (III) and Yb (II) molecular nanomagnets in metal-organic chains functionalized by octacyanidometallates (IV) Inorg. Chem. Front. 6 2423
[22] Yu Z and Yang Y 2019 White up-conversion efficiency of Yb3+/Er3+ /Tm3+ co-doped β-NaYF4 nano-crystals J. Lumin. 207 48
[23] Li H, Xu L and Chen G 2017 Controlled synthesis of monodisperse hexagonal NaYF4:Yb/Er nanocrystals with ultrasmall size and enhanced up conversion luminescence Molecules 22 2113
[24] You W, Tu D and Chen X 2019 ‘Chameleon-like’ optical behavior of lanthanide-doped fluoride nanoplates for multilevel anti-counterfeiting applications Nano Res. 12 1417
[25] Acar Y, Coban M B, Gungor E and Kara H 2020 Two new NIR luminescent Er (III) coordination polymers with potential application optical amplification devices J. Cluster Sci. 31 117
[26] Tian X, Dou H and Wu L 2019 Photoluminescence and thermometry properties of up conversion phosphor NaBiF$_4$:Yb$^{3+}$/Tm$^{3+}$ Opt. Mater. 99 109544
[27] Priya R, Pandey O P and Dhoble S J 2021 Review on the synthesis, structural and photo-physical properties of Gd$_2$O$_3$ phosphors for various luminescent applications—ScienceDirect Opt. & Laser Technol. 135 106663
[28] Feng J and Zhang H 2013 Hybrid materials based on lanthanide organic complexes: a review Chem. Soc. Rev. 42 387
[29] He H Y et al 2015 La-doping content effect on the optical and electrical properties of La-doped ZnO thin films J. Mater. Sci. Mater. El 26 1205
[30] Wang Z et al 2021 Microsized red luminescent MgAl$_2$O$_4$:Mn$^{4+}$ single-crystal phosphor grown in molten salt for white LEDs Inorg. Chem. 59 18374
[31] Ding B et al 2018 Large-pore mesoporous-silica-coated upconversion nanoparticles as multifunctional Immunoadjuvants with ultrahigh photosensitizer and antigen loading efficiency for improved cancer photodynamic immunotherapy Adv. Mater. 30 1802479
[32] Hoerder G J et al 2019 Sr$_2$Al$_2$O$_4$:Eu$^{2+}$ - a high performance red phosphor to brighten the future Nat. Commun. 10 1824
[33] Wang Q, Liu M, Liu Q, Xiong M, Xiong Z and Wu F 2021 A review on fluorescence intensity ratio thermometer based on rare-earth and transition metal ions doped inorganic luminescent materials J. Alloys Compd. 850 156744
[34] Zhou J, Liu Q, Feng W, Sun Y and Li F 2015 Upconversion luminescent materials: advances and applications Chem. Rev. 115 395–465
[35] Tang Y, Wu H, Cao W, Cui Y and Qian G 2020 Luminescent metal–organic frameworks for white LEDs Adv. Opt. Mater. 2001817
[36] Bao N et al 2016 Construction of ordered mesoporous (Eu–La)/ZnO composite material and its luminescent characters J. Lumin. 177 409
[37] Bazzi R et al 2004 Synthesis and properties of europium-based phosphors on the nanometer scale: Eu$_2$O$_3$, Gd$_2$O$_3$: Eu, and Y$_2$O$_3$: Eu J. Collid Interface Sci. 273 191
[38] Zatsopin A and Kuznetsova Y 2020 Kinetic selection of nonradiative excitation in photonic nanoparticles Gd$_2$O$_3$: Er Phys. Chem. Chem. Phys. 22 6818
[39] Gangwar J, Gupta B K, Tripathi S K and Sevastava A K 2015 Phase dependent thermal and spectroscopic responses of Al$_2$O$_3$ nanostructures with different morphogenesis Nanoscale 7 13313
[40] Pierre A C and Pajonk G M 2002 Chemistry of aerogels and their applications Chem. Rev. 102 4243
[41] Liu H, Geng B, Chen Y and Wang H 2017 Review on the aerogel-type oil sorbents derived from nanocellulose ACS Sustainable Chem. Eng. 5 49
[42] Lu Z, Yuan Z, Liu Q, Hu Z, Xie F and Zhu M 2013 Multi-scale simulation of the tensile properties of fiber-reinforced silica aerogel composites Mater. Sci. Eng. A 625 278
[43] Wang F et al 2020 In situ synthesis of biomimetic silica nanofibrous aerogels with temperature-invariant superelasticity over one million compressions Angew. Chem. Int. Ed. 59 8283
[44] He F et al 2020 Alumina aerogels with unidirectional aligned channels under different freezing temperatures during freeze casting: Part II: anisotropic mechanical and thermal conductive properties Ceram. Int. 46 25691
[45] Jia H, Liu S, Mao Z and Wang D 2021 Preparation and properties of the Al$_2$O$_3$–SiO$_2$ aerogel/alumina framework composite Ceram. Int. 47 1466
[46] Cheng W, Rechberger F and Niederberger M 2016 Three-dimensional assembly of yttrium oxide nanosheets into luminescent aerogel monoliths with outstanding adsorption properties ACS Nano 10 2467
[47] Zhang W, Liu Y, Yu H and Dong X 2019 Eu and Tb co-doped porous SiO$_2$ aerogel composite and its luminescent properties J. Photochem. Photobiol. A 379 47
[48] Gaponik N, Wolf A, Marx R, Lesnyak V, Schilling K and Eychmüller A 2008 Three-dimensional self-assembly of thiol–capped CdTe nanocrystals: gels and aerogels as building blocks for nanotechnology Adv. Mater. 20 4257
[49] Meza O, Villalba-Leal E G, Diaz-Torres L A, Desirena H, Rodriguez-López J I and Pérez E 2014 Luminescence concentration quenching mechanism in Gd$_2$O$_3$: Eu$^{3+}$ J. Phys. Chem. A 118 1390