A comparative study of ZnAl$_2$O$_4$ nanoparticles synthesized from different aluminum salts for use as fluorescence materials

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Three ZnAl$_2$O$_4$ samples were prepared via a modified polyacrylamide gel method using a citric acid solution with different aluminum salt starting materials, including AlCl$_3$·6H$_2$O, Al$_2$(SO$_4$)$_3$·18H$_2$O, and Al(NO$_3$)$_3$·9H$_2$O under identical conditions. The influence of different aluminum salts on the morphologies, phase purity, and optical and fluorescence properties of the as-prepared ZnAl$_2$O$_4$ nanoparticles were studied. The experimental results demonstrate that the phase purity, particle size, morphology, and optical and fluorescence properties of ZnAl$_2$O$_4$ nanoparticles can be manipulated by the use of different aluminum salts as starting materials. The energy bandgap (E$_g$) values of ZnAl$_2$O$_4$ nanoparticles increase with a decrease in particle size. The fluorescence spectra show that a major blue emission band around 400 nm and two weaker side bands located at 410 and 445 nm are observed when the excitation wavelength is 325 nm. The ZnAl$_2$O$_4$ nanoparticles prepared from Al(NO$_3$)$_3$·9H$_2$O exhibit the largest emission intensity among the three ZnAl$_2$O$_4$ samples, followed in turn by the ZnAl$_2$O$_4$ nanoparticles prepared from Al$_2$(SO$_4$)$_3$·18H$_2$O and AlCl$_3$·6H$_2$O. These differences are attributed to combinational changes in E$_g$ and the defect types of the ZnAl$_2$O$_4$ nanoparticles.

Spinel ZnAl$_2$O$_4$ is known to have a wide energy bandgap (E$_g$), high mechanical resistance, high fluorescence efficiency, high chemical and thermal stability, high photocatalytic activity, and low surface acidity, all of which make it a suitable material for a wide range of applications, including use in photoelectronic devices, catalysts, electroluminescence displays, stress imaging devices, optical coatings, and highly efficient phosphors$^{1-5}$. Based on the above mentioned applications, various morphologies of spinel ZnAl$_2$O$_4$ have been prepared, including one-dimensional microfibers, porous structures, nanoparticles, nanorods, nanotubes, and so on$^{4-8}$. It has been noted that the optical properties of these materials are strongly dependent on their morphologies and preparation methods. In particular, ZnAl$_2$O$_4$ nanostructures are expected to exhibit enhanced optical and fluorescence properties usually absent in bulk ZnAl$_2$O$_4$. Therefore, the preparation and study of the optical and fluorescence properties of ZnAl$_2$O$_4$ nanostructure powder is of great interest.

Spinel ZnAl$_2$O$_4$ semiconductors have been synthesized using a variety of different methods, such as the solid-state reaction method$^{9,10}$, a self-generated template pathway$^9$, the combustion synthesis route$^{11}$, the sol–gel method$^{12}$, a co-precipitation approach$^9$, the polymeric precursor method$^{13}$, the citrate precursor method$^4$, a hydrothermal process$^7$, a solvothermal approach$^{14}$, and the microwave-hydrothermal route$^{15}$. The particle size of ZnAl$_2$O$_4$ has a large effect on its optical and fluorescence properties. Generally,
smaller particles have a relatively larger specific surface area, and therefore have a larger amount of dangling and unsaturated bonds on the particle surface. This in turn affects the defect levels and fluorescence properties of the powder. However, the main disadvantage of preparing spinel \( \text{ZnAl}_2\text{O}_4 \) by the traditional synthesis routes, such as the co-precipitation approach, the solid-state reaction method, and others, is the large particle size of the product.

The polyacrylamide gel route is a very good sol-gel method for the preparation of superfine nanoparticles. Appropriate selection of a chelating agent, monomer systems, initiator, pH value, and sintering temperature can significantly improve the quality of the prepared nanoparticles. In addition, different aluminum salts, i.e. different anionic species in the precursor solutions, can greatly influence the morphology, phase purity, and optical and fluorescence properties of the \( \text{ZnAl}_2\text{O}_4 \). However, most previously reported studies have only used a single aluminum salt as a starting material and have not investigated the influences of different aluminum salts on the morphology, structure, and optical and fluorescence properties of the obtained \( \text{ZnAl}_2\text{O}_4 \).

In this study, three different aluminum salts are used as starting materials to synthesize three \( \text{ZnAl}_2\text{O}_4 \) gels via a polyacrylamide gel route, specifically aqueous solutions of citric acid with \( \text{Al}_2(\text{SO}_4)_3\cdot18\text{H}_2\text{O} \), \( \text{AlCl}_3\cdot6\text{H}_2\text{O} \), or \( \text{Al(NO}_3)_3\cdot9\text{H}_2\text{O} \) were used under identical conditions. In order to obtain superfine nanoparticles, \( \text{N,N’-methylene-bisacrylamide} \) was used as a cross-linking agent, and glucose was used to prevent gel collapse. After sintering these xerogels, three \( \text{ZnAl}_2\text{O}_4 \) nanostructure samples were obtained. Their phase purity, morphologies, and optical and fluorescence properties were then characterized and compared. The objective of the present work is to investigate the influence of different aluminum salt starting materials on the resulting \( \text{ZnAl}_2\text{O}_4 \) nanostructures and on their optical and fluorescence properties.

## Results

The obtained \( \text{ZnAl}_2\text{O}_4 \) xerogels decomposed into products after being sintered at 600°C for 5h in air. Figure 1 shows the XRD patterns of \( \text{ZnAl}_2\text{O}_4 \) nanoparticles prepared from (S1) \( \text{Al}_2(\text{SO}_4)_3\cdot18\text{H}_2\text{O} \), (S2) \( \text{AlCl}_3\cdot6\text{H}_2\text{O} \), and (S3) \( \text{Al(NO}_3)_3\cdot9\text{H}_2\text{O} \). It can be seen that samples S1 and S2 have crystallized in a single phase with a spinel structure and with space group O7h, but sample S3 contains small amounts of \( \text{ZnO} \) (JCPDS card No. 36–1451) impurities in addition to the major phase of spinel \( \text{ZnAl}_2\text{O}_4 \) structure (JCPDS card No. 05–0669). According to the literature, the relevant reactions can be described by the following equations:

\[
4\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + 4\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} + 4\text{C}_6\text{H}_4\text{O}_7 + 4\text{C}_4\text{H}_2\text{O}_6 + 4\text{C}_4\text{H}_2\text{ON}
+ 4\text{C}_7\text{H}_{16}\text{N}_2\text{O}_2 + 4\text{NH}_3 \cdot \text{H}_2\text{O} + 75\text{O}_2 \rightarrow 4\text{ZnAl}_2\text{O}_4 + 10\text{N}_2 + 88\text{CO}_2 + 170\text{H}_2\text{O}
+ 12\text{SO}_2 + 4\text{NH}_3
\]

(1)

\[
4\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + 8\text{AlCl}_3 \cdot 6\text{H}_2\text{O} + 4\text{C}_6\text{H}_4\text{O}_7 + 4\text{C}_4\text{H}_2\text{O}_6 + 4\text{C}_3\text{H}_5\text{ON} + 4\text{C}_7\text{H}_{16}\text{N}_2\text{O}_2
+ 24\text{NH}_3 \cdot \text{H}_2\text{O} + 81\text{O}_2 \rightarrow 4\text{ZnAl}_2\text{O}_4 + 10\text{N}_2 + 88\text{CO}_2 + 154\text{H}_2\text{O} + 24\text{NH}_3
+ 24\text{HCl}
\]

(2)
For samples S1 and S2, the observed diffraction peaks at $2\theta$ are 31.22, 36.77, 44.69, 48.98, 55.52, 59.27, 65.06, 73.97, and 77.12 and can be ascribed, respectively, to the (220), (311), (400), (331), (422), (511), (440), (620), and (533) planes of ZnAl$_2$O$_4$. The mean grain size of samples S1, S2, and S3 were quantitatively evaluated based on the line broadening of the (220), (311), (511), and (440) peaks using the Scherrer formula, to be 13, 16, and 24 nm, respectively. XRD results indicate that the choice of the aluminum salts also has an influence on the phase purity of the final product. A possible reason for the formation of impurity phases when using citric acid as a chelating agent is that citric acid has a relatively weak coordinating capacity toward the metal ion of Al(NO$_3$)$_3$ $\cdot$ 9H$_2$O, and hence the formed metal complexonate is not expected to be highly stable.

Fourier transform infrared (FT-IR) spectra of the ZnAl$_2$O$_4$ nanoparticles prepared from (S1) Al$_2$(SO$_4$)$_3$ $\cdot$ 18H$_2$O, (S2) AlCl$_3$ $\cdot$ 6H$_2$O, and (S3) Al(NO$_3$)$_3$ $\cdot$ 9H$_2$O are shown in Fig. 2. The FT-IR spectra show a series of absorption peaks in the range of 400–2000 cm$^{-1}$. According to the specific frequencies of the absorption peaks, the functional groups existing in the samples can be deduced. Peaks at 1633, 656, 552, and 493 cm$^{-1}$ are present in all samples, and are assigned to the H-O-H bending vibration of adsorbed water$^{19}$, Al-O symmetric stretching vibration ($\nu_1$)$^{19-22}$, Al-O symmetric bending vibration ($\nu_2$)$^{19-22}$, and Al-O asymmetric stretching vibration ($\nu_3$)$^{21,22}$, respectively. For sample S2, the peaks located at 1186 and 1117 cm$^{-1}$ are attributed to the S=O asymmetric stretching vibration$^{23}$ and the S-O symmetric stretching vibration$^{23,24}$, respectively.

Figure 3 shows the TG/DTA curves of the ZnAl$_2$O$_4$ xerogels obtained from (S1) Al$_2$(SO$_4$)$_3$ $\cdot$ 18H$_2$O, (S2) AlCl$_3$ $\cdot$ 6H$_2$O, and (S3) Al(NO$_3$)$_3$ $\cdot$ 9H$_2$O. There are four weight loss stages observed for each sample. The first weight loss stage is seen at a low temperature range (before 200 °C) and corresponds to the evaporation of surface water in the ZnAl$_2$O$_4$ xerogel precursors$^{25,26}$. The second weight loss stage (around 200–250 °C) is due to the evaporation of structural water$^{25,26}$. The third weight loss stage (between 250–400 °C) is due to the decomposition of small molecular organic compounds. The largest and final weight loss stage (around 400–620 °C) is due to decomposition of complexes, glucose, and the polyacrylamide side-chain, as well as combustion of the polyacrylamide backbone and other residues$^{27,28}$. The total weight loss measured for the ZnAl$_2$O$_4$ xerogel precursors were 97.31% for (S1) Al$_2$(SO$_4$)$_3$ $\cdot$ 18H$_2$O, 95.201% for (S2) AlCl$_3$ $\cdot$ 6H$_2$O, and 98.234% for (S3) Al(NO$_3$)$_3$ $\cdot$ 9H$_2$O. In Fig. 3 (S1), the main endothermic peak appeared at around 535 °C and corresponds to the thermal decomposition of the complexes, polyacrylamide backbone, and other residues originating from Al$_2$(SO$_4$)$_3$ $\cdot$ 18H$_2$O. Meanwhile, the main endothermic peaks appeared at 557 °C (Fig. 3(S2)) for the ZnAl$_2$O$_4$ xerogel precursor obtained from AlCl$_3$ $\cdot$ 6H$_2$O, and at 528 °C (Fig. 3(S3)) for (S3) Al(NO$_3$)$_3$ $\cdot$ 9H$_2$O. The slightly different decomposition temperatures of the three ZnAl$_2$O$_4$ xerogels may be related to differences in the microstructures caused by the presence of different anionic species (Cl$^-$, SO$_4^{2-}$, and NO$_3^-$) in the synthesis process. The chemical reaction is complete at ~600/620 °C and results in the formation of ZnAl$_2$O$_4$ nanoparticles. However, for ZnAl$_2$O$_4$...
nanoparticles prepared from Al₂(SO₄)₃·18H₂O, a higher heat treatment temperature is usually needed to improve the phase purity.

To confirm whether the formation of ZnAl₂O₄ nanoparticles prepared from Al₂(SO₄)₃·18H₂O needed a higher heat treatment temperature, FT-IR measurements were carried out using a Bruker IFS 66 v/S spectrometer. The FT-IR spectra of the ZnAl₂O₄ xerogel prepared from Al₂(SO₄)₃·18H₂O and sintered at different temperatures are presented in Fig. 4. Here it can be seen that the S=O asymmetric stretching vibration (1186 cm⁻¹) and S-O symmetric stretching vibration (1117 cm⁻¹) peak intensities decrease with the increase of sintering temperature. This result indicates that the SO₄²⁻ anion coordinates to Zn and Al cations and forms a bridged bidentate structure²³,²⁹,³⁰.

In the case of the sample obtained by sintering the xerogel at 900°C, all of the organic peaks disappear except for the H—O—H peak (1633 cm⁻¹). These results indicate that the effects of aluminum salts and sintering temperature on the phase purity of ZnAl₂O₄ cannot be neglected. Based on the subtle information gathered from the XRD and FT-IR results, the relevant reactions can be described as follows:

Figure 3. TG/DTA curves of ZnAl₂O₄ xerogel prepared from (S1)Al₂(SO₄)₃·18H₂O, (S2) AlCl₃·6H₂O, and (S3) Al(NO₃)₃·9H₂O.
The results indicate that the reaction (1) cannot occur at 600 °C, and that a higher sintering temperature is needed for the formation of pure ZnAl$_2$O$_4$ nanoparticles.

In order to investigate the effects of different aluminum salts on the formation of ZnAl$_2$O$_4$, including the particle size and surface morphology, SEM and TEM images were collected of the ZnAl$_2$O$_4$ samples prepared using different aluminum salts and sintered at 700 °C, and are shown in Fig. 5 and Fig. 6. The SEM images of the ZnAl$_2$O$_4$ samples reveal that the particles are almost spherical in shape and have a narrow particle size distribution (Fig. 5(S1–S3)). When AlCl$_3$·6H$_2$O is added into the ZnAl$_2$O$_4$ precursor, large particles form, however, if Al$_2$(SO$_4$)$_3$·18H$_2$O is added into the precursor, small particles with little adhesion are observed, as shown in Fig. 5(S1-S2).

Figure 6 shows (S1–S3) TEM image, (SH1- SH3) HRTEM image, and (SP1–SP3) the particle size distribution of ZnAl$_2$O$_4$ nanoparticles prepared from (S1) Al$_2$(SO$_4$)$_3$·18H$_2$O, (S2) AlCl$_3$·6H$_2$O, and Al(NO$_3$)$_3$·9H$_2$O. The ZnAl$_2$O$_4$ nanoparticles are spherical in shape with a narrow particle size distribution, as shown in Fig. 6(S1–S3). The corresponding particle size distribution patterns are given in the Fig. 6 (SP1–SP3). The average particle sizes of samples S1, S2, and S3 are around 12, 18, and 24 nm, respectively. TEM results show that the particle size variation tendencies for samples S1, S2, and S3 are consistent with those calculated from XRD patterns (Fig. 1). In addition, the BET surface area of the sample decreases with the increase of particle size as shown in Table 1. Compared with sample S2, the average particle size and BET surface area of sample S1 is significantly reduced, an effect which may be due to the SO$_4^{2−}$ anion forming a bridged bidentate structure. Fig. 6(S2) inset presents the SAED pattern taken from a portion of the ZnAl$_2$O$_4$ nanoparticles shown in Fig. 6(S2). The associated electron diffraction pattern is consistent with that of pure ZnAl$_2$O$_4$ crystals of a spinel structure, indexed as shown in Fig. 7(a). The SAED pattern revealed that the ZnAl$_2$O$_4$ nanoparticles possess interplanar spacings of 2.8235, 2.4156, 2.0205, 1.6328, 1.5531, and 1.4203 Å corresponding to the (220), (311), (400), (422), (511), and (440) planes, respectively.

Figure 6 (SH1)-(SH3) shows the HRTEM image of ZnAl$_2$O$_4$ nanoparticles prepared from (S1) Al$_2$(SO$_4$)$_3$·18H$_2$O, (S2) AlCl$_3$·6H$_2$O, and (S3) Al(NO$_3$)$_3$·9H$_2$O. For these samples, the lattice planes of ZnAl$_2$O$_4$ nanoparticles were (111) with a lattice space of 4.6687 Å, (220) with a lattice space of 2.8437 Å, (222) with a lattice space of 2.3345 Å, (400) with a lattice space of 2.0210 Å, (331) with a lattice space of 1.8550 Å, and (440) with a lattice space of 1.4356 Å. It has been noted that (111), (220), (222), (400), (331) and (440) planes can be attributed to spinel ZnAl$_2$O$_4$ structure corresponding to JCPDS card No. 05-0669.

Figure 7(a) shows the UV-Vis diffuse reflectance spectra of ZnAl$_2$O$_4$ samples prepared from (S1) Al$_2$(SO$_4$)$_3$·18H$_2$O, (S2) AlCl$_3$·6H$_2$O, and (S3) Al(NO$_3$)$_3$·9H$_2$O. Considering that ZnAl$_2$O$_4$ is a direct band-gap semiconductor, the Eg of the ZnAl$_2$O$_4$ samples can be estimated from plots of $(\alpha h\nu)^2$ versus $h\nu$. 

The reaction (1) can be written as:

$$4\text{Zn(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} \cdot 4\text{Al}_2\text{(SO}_4\text{)}_3 \cdot 1\text{8H}_2\text{O} \cdot 4\text{C}_6\text{H}_8\text{O}_7 \cdot 4\text{C}_6\text{H}_{12}\text{O}_6 \cdot 4\text{C}_3\text{H}_2\text{ON}$$

$$+ 4\text{C}_7\text{H}_6\text{N}_2\text{O}_3 \cdot 4\text{NH}_3 \cdot \text{HO}_2 + 79\text{O}_2 \xrightarrow{600-800^\circ\text{C}} 4\text{SO}_4^{2−} / \text{ZnAl}_2\text{O}_4 + 10\text{N}_2 + 88\text{CO}_2 + 170\text{H}_2\text{O} + 8\text{SO}_2 + 4\text{NH}_4$$

The results indicate that the reaction (1) cannot occur at 600 °C, and that a higher sintering temperature is needed for the formation of pure ZnAl$_2$O$_4$ nanoparticles.

The reaction (1) can be written as:

$$\text{SO}_4^{2−} / \text{ZnAl}_2\text{O}_4 \xrightarrow{900^\circ\text{C}} \text{ZnAl}_2\text{O}_4 + \text{SO}_2 + \text{O}_2$$
using the Tauc relation\textsuperscript{33}. This is shown in Fig. 7(b), where $h$ is the Planck constant, $\alpha$ is the Kubelka-Munk (K–M) absorption coefficient, and $\nu$ is the frequency. The linear portions of the plots are extrapolated to the $h\nu$ axis to give the values of $E_g$. The calculated $E_g$ values of samples S1, S2, and S3 are $3.98 \pm 0.01$, $3.92 \pm 0.01$ and $3.22 \pm 0.01$ eV, respectively. Generally, the $E_g$ values of nano-sized semiconductors increase with a decrease in particle size. In this case, the observed phenomenon is consistent with what has been previously reported.

Figure 5. SEM images and particle size distribution of ZnAl\textsubscript{2}O\textsubscript{4} xerogel prepared from (S1) Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}∙18H\textsubscript{2}O, (S2) AlCl\textsubscript{3}∙6H\textsubscript{2}O, and (S3) Al(NO\textsubscript{3})\textsubscript{3}∙9H\textsubscript{2}O and sintered at 700°C.
Figure 8(a) show the fluorescence spectra of ZnAl$_2$O$_4$ samples prepared from (S1) Al$_2$(SO$_4$)$_3$∙18H$_2$O, (S2) AlCl$_3$∙6H$_2$O, and (S3) Al(NO$_3$)$_3$∙9H$_2$O and sintered at 700°C. The fluorescence spectra with a wavelength range of 385 ~ 445 nm for all samples are presented after excitation with light, $\lambda_{\text{exc}} = 325$ nm. The fluorescence spectrum of the ZnAl$_2$O$_4$ sample is wide and can be resolved using three Gaussian peaks at 400, 410, and 445 nm (Fig. 8b). The three emission peaks at 400, 410, and 445 nm can be ascribed to intra band gap defects such as oxygen vacancies.[34] It has been noted that there is an obvious increase in the fluorescence intensity of the peak located at 400 nm when the $E_g$ value decreases (see Fig. 8(a) inset).

Figure 6. (S1–S3) TEM image, (SH1- SH3) HRTEM image, and (SP1–SP3) Particle size distribution of ZnAl$_2$O$_4$ nanoparticles prepared from (S1) Al$_2$(SO$_4$)$_3$∙18H$_2$O, (S2) AlCl$_3$∙6H$_2$O, and (S3) Al(NO$_3$)$_3$∙9H$_2$O and sintered at 700°C. The inset presents the SAED pattern taken from a portion of the ZnAl$_2$O$_4$ nanoparticles shown in Fig. 6(S2).

| Sample | Crystallite size (nm) | Particle size (nm) | $E_g$ (eV) | BET specific surface area $(m^2/g)$ |
|--------|-----------------------|-------------------|-----------|-----------------------------------|
| S1     | 13                    | 12                | 3.98      | 40.13                             |
| S2     | 16                    | 18                | 3.92      | 27.75                             |
| S3     | 24                    | 24                | 3.22      | 19.38                             |

Table 1. Crystallite size, particle size, $E_g$ and BET specific surface area of samples S1, S2 and S3.
Compared with the ZnAl$_2$O$_4$ nanoparticles prepared from Al$_2$(SO$_4$)$_3$·18H$_2$O, the ZnAl$_2$O$_4$ nanoparticles obtained from AlCl$_3$·6H$_2$O have a smaller $E_g$ value, however, their fluorescence intensity is also smaller. Therefore, in this case we cannot simply attribute the differences in the fluorescence intensity for the three ZnAl$_2$O$_4$ samples only to the differences in their $E_g$ values. The difference in the fluorescence intensity of the two ZnAl$_2$O$_4$ samples may also be related to the different phase purities of ZnAl$_2$O$_4$ samples prepared from (S1) Al$_2$(SO$_4$)$_3$·18H$_2$O and (S2) AlCl$_3$·6H$_2$O. In the case of the ZnAl$_2$O$_4$ sample prepared from Al$_2$(SO$_4$)$_3$·18H$_2$O, traces of the $S\equiv O$ and $S-O$ are visible in the FT-IR spectrum after sintering at 700 °C.

Discussion

In order to understand the fluorescence mechanism of the prepared ZnAl$_2$O$_4$ samples, it is necessary to propose a schematic band diagram to illustrate the process of excitation and emission for the system. Figure 9 shows a schematic band diagram for the fluorescence mechanism of ZnAl$_2$O$_4$ samples obtained from (S1) Al$_2$(SO$_4$)$_3$·18H$_2$O, (S2) AlCl$_3$·6H$_2$O, and (S3) Al(NO$_3$)$_3$·9H$_2$O. It is known that Al$^{3+}$ 2$p$ orbitals and $s$ orbitals located at the upper part of the Al$^{3+}$ 2$p$ orbitals make up the major conduction band (CB) edge of ZnAl$_2$O$_4$, and the hybridization band composed of O$^{2-}$ 2$p$ and Zn$^{2+}$ 3$d$ orbitals makes up the upper valence band (VB) [35]. When the $E_g$ value $>\lambda_{\text{exc}}$ (3.82 eV vs. 325 nm) it can be seen that one electron transition occurs from VB onto the intra band gap defects (IBGD) energy level (Fig. 9(S1) and (S2)). After that, the electron will be driven by continued transition from IBDG to CB. Then, the electron on the CB drops down to the low energy level through loss of energy by vibration relaxation (VR). Finally, the electron on the low energy level undergoes a radiative recombination with a hole in the valence band, accompanied by three blue-light emissions. For sample S1, the impurity (SO$_4^{2-}$) plays a crucial role to...
promote the electron transition from IL (impurity level) to CB and improve the fluorescence properties. When $E_g < \lambda_{\text{exc}}$, one electron transition occurs from the VB to the high energy level (Fig. 9(S3)). Then, the electron on the high energy level drops down to the CB by internal conversion. At the same time, the electron on the CB by VR drops down to the low energy level with an accompanying loss of energy. Finally, the electron on the low energy level undergoes a radiative recombination with a hole in the valence band, accompanied by a series of blue-light emissions.

Figure 10 shows the Commission International De l’Eclairage (CIE) diagram of a ZnAl$_2$O$_4$ phosphor under 325 nm laser excitations. The CIE color coordinates ($x$, $y$) of the ZnAl$_2$O$_4$ phosphor was calculated using the fluorescence spectra. A typical CIE color coordinate of a ZnAl$_2$O$_4$ phosphor was found to be $x$, $y$ equals 0.1729, 0.0048 respectively under 325 nm laser excitations.

According to equation (7), the fluorescence quantum efficiency of the ZnAl$_2$O$_4$ phosphor can be calculated from the experimental data.

$$\text{QE}_s = \text{QE}_{s-s} \times \frac{\int I_s}{\int I_{s-s}} \times \frac{A_s - s}{A_s}$$

Where $\text{QE}_s$ and $\text{QE}_{s-s}$ are the fluorescence quantum efficiencies of the prepared sample and standard sample, respectively, under an excitation wavelength of 325 nm. $\int I_s$ and $\int I_{s-s}$ are the integrated emission intensities of the prepared sample and standard sample under an excitation wavelength of 325 nm. $A_s$ and $A_{s-s}$ are the absorbance of the prepared sample and standard sample under an excitation wavelength of 325 nm. The standard sample is 5-sulfosalicylic acid, which has a quantum efficiency of about 58% under an excitation wavelength of 325 nm. The fluorescence quantum efficiencies of samples S1, S2, and S3 were calculated to be 6.38%, 4.24%, and 10.11%, respectively. Observations made during these experiments show that the spinel ZnAl$_2$O$_4$ phosphor could be useful for blue light-emitting materials.

In summary, ZnAl$_2$O$_4$ nanoparticles with different particle sizes were prepared using a modified polyacrylamide gel route from different aluminum salt starting materials: Al$_2$(SO$_4$)$_3$-18H$_2$O, AlCl$_3$-6H$_2$O, and Al(NO$_3$)$_3$-9H$_2$O. The type of aluminum salt used can markedly influence the phase purity, particle size, and fluorescence properties of the resulting ZnAl$_2$O$_4$ phosphors.
Figure 9. Fluorescence mechanism of ZnAl$_2$O$_4$ samples prepared from (S1) Al$_2$(SO$_4$)$_3$∙18H$_2$O, (S2) AlCl$_3$∙6H$_2$O, and (S3) Al(NO$_3$)$_3$∙9H$_2$O.

Figure 10. CIE diagram of ZnAl$_2$O$_4$ phosphor under 325 nm laser excitations.
Table 2. Starting compositions of samples S1, S2 and S3.

| Sample | Al2(SO4)3·18H2O | AlCl3·6H2O | Al(NO3)3·9H2O | Zn(NO3)2·6H2O | citric acid | glucose | acrylamide | Bis-acrylamide |
|--------|-----------------|------------|---------------|----------------|-------------|---------|------------|----------------|
| S1     | 6.664g          | /          | /             | 1.4875g        | 4.7282g     | 20g     | 9.5958g    | 1.9192g        |
| S2     | /               | 2.4143g    | /             | 1.4875g        | 4.7282g     | 20g     | 9.5958g    | 1.9192g        |
| S3     | /               | /          | 3.7513g       | 1.4875g        | 4.7282g     | 20g     | 9.5958g    | 1.9192g        |

size, and optical and fluorescence properties of the final product. Under 325 nm excitation, samples of ZnAl2O4 phosphor show blue emissions and the CIE colour coordinate was found to be (0.1729, 0.0048). The fluorescence mechanisms of the ZnAl2O4 phosphor have been discussed based on the experimental results. The fluorescence experiments revealed that the as-prepared ZnAl2O4 phosphor exhibits interesting abilities for application in blue light-emitting materials. Interestingly, similar preparation methods may be employed for the synthesis of other metal oxides nanoparticles, including fluorescence materials, multiferroic materials, oxide thermoelectric materials, photocatalytic materials, solid oxide fuel cell materials, and high-temperature superconducting materials.

Methods

Materials. Zn(NO3)2·6H2O, AlCl3·6H2O, Al2(SO4)3·18H2O, and Al(NO3)3·9H2O were purchased from DaMao Chem. Ltd., Tianjing. Citric acid (C₆H₈O₇, AR), glucose (C₆H₁₂O₆·H₂O, 99%), acrylamide (C₃H₅NO, AR), and N, N’-methylene-bisacrylamide (C₇H₁₀N₂O₂, 99%) were purchased from Kemiou Chem. Ltd., Tianjing and used without further purification.

Synthesis. A certain stoichiometric amounts of Zn(NO3)2·6H2O and different aluminum salts (Al2(SO4)3·18H2O, AlCl3·6H2O, and Al(NO3)3·9H2O) were labeled sample S1, S2 and S3, respectively) were dissolved in the deionized water to obtain a final solution of 0.015 mol/L with the total cations. Starting compositions of samples S1, S2 and S3 are given in Table 2. After the solution was transparent, a stoichiometric amount of chelating agent (citric acid) was added into the solution in the mole ratio 1.5:1 with respect to the total cations (Zn²⁺ and Al³⁺) to complex the cations. After that, 20 g glucose was dissolved into the solution. Finally, the acrylamide and N, N’-methylene-bisacrylamide monomers were added into the solution. The resultant solution was heated to 90°C on a hot plate to initiate the polymerization reaction, and a few minutes later a polycrystalline gel was formed. The gel was dried at 120°C for 24 h in a thermostat drier. The obtained xerogel precursor was ground into powder and some powder was sintered at 600, 700, 800, and 900°C for 5 h in air to prepare the objective products.

Sample characterization. The ZnAl2O4 xerogel precursor sintered at 600 and 700°C were analyzed by X-ray diffractometer (DX-2700) with Cu Kα radiation. Fourier transform infrared (FTIR) spectra in the range 400–2000 cm⁻¹ were recorded using a Bruker IFS 66 v/S spectrometer. Thermogravimetric (TG) and differential thermal analysis (DTA) analyses were performed in a SDT Q600 (TA instruments, Inc. USA) simultaneous thermal analyzer at a heating rate of 10°C/min. The surface morphology of the synthesized ZnAl2O4 sample was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The surface area of the samples were characterized by a 3H-2000BET-M instrument. The absorption spectra of the samples were examined on a Shimadzu UV-2500 UV-Visible spectrophotometer. The fluorescence spectra were collected at room temperature in a confocal Raman system using a He-Cd laser (325 nm, RGB laser system, NovaPro 30 mW, Germany).

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et al.: Wang, S.-F. A comparative study of ZnAl$_2$O$_4$ nanoparticles synthesized from different aluminum salts for use as fluorescence materials. 

**Acknowledgements**

This work was supported by the NSAF joint Foundation of China (U1330103) and by Outstanding Doctoral Student Support Plan (A1098524023901001074).

**Author Contributions**

S.W. and G.S. contributed to the preparation and characterization of the nanoparticles. L.L. measured the fluorescence spectra. S.W., G.S., L.F. and X.X. analyzed data from experiments and wrote the main manuscript. X.Z. led the project.

**Additional Information**

**Competing financial interests:** The authors declare no competing financial interests.

**How to cite this article:** Wang, S.-F. et al. A comparative study of ZnAl$_2$O$_4$ nanoparticles synthesized from different aluminum salts for use as fluorescence materials. *Sci. Rep.* 5, 12849; doi: 10.1038/srep12849 (2015).