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# Synthesis and optical properties of chromium-doped spinel hollow nanofibers by single-nozzle electrospinning

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Novel spinel hollow nanofibers were synthesized by a convenient single-nozzle electrospinning technique. Based on the composition and morphology results by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM), a 'gas-push' model was proposed to elucidate the formation mechanism of hollow nanofibers during calcination. Photoluminescence (PL) properties of calcined ZnAl<sub>2</sub>O<sub>4</sub>:  $xCr^{3+}$  and MgAl<sub>2</sub>O<sub>4</sub>:  $xCr^{3+}$  nanofibers were investigated systematically. Under an excitation of 400 nm or 530–550 nm (<sup>4</sup>A<sub>2g</sub>→<sup>4</sup>T<sub>1g</sub> or <sup>4</sup>A<sub>2g</sub>→<sup>4</sup>T<sub>2g</sub> transitions of Cr<sup>3+</sup> ions), an emission band at 675–725 nm including a sharp emission line (R-line) at ~687 nm with several vibrational sidebands was obtained. Compared with the spectroscopic properties of ZnAl<sub>2</sub>O<sub>4</sub>:  $xCr^{3+}$  nanofibers. By calculation of crystal field strength, the value of  $D_q/B$  is estimated to be 3.25 and 2.72 for ZnAl<sub>2</sub>O<sub>4</sub>:  $xCr^{3+}$  and MgAl<sub>2</sub>O<sub>4</sub>:  $xCr^{3+}$  nanofibers, respectively. The difference of crystal field strength gives a good explanation of the spectroscopic and decay evolution between ZnAl<sub>2</sub>O<sub>4</sub>:  $xCr^{3+}$  and MgAl<sub>2</sub>O<sub>4</sub>:  $xCr^{3+}$  nanofibers,

### 1. Introduction

Light-emitting nanostructured materials with dimensional restriction have attracted much attention due to their applications in panel displays, lighting, lasing, waveguides, sensors, biological markers, *etc.*<sup>1–7</sup> Owing to their superior chemical and thermal stability, oxide-based phosphors have gained more interest compared with other fluorides, sulfides, oxysulfides, *etc.*<sup>8–14</sup> When the size of phosphors is reduced to the nanoscale, the luminescence quantum field and display resolution is expected to be greatly improved. Among various oxide hosts, a spinel (ZnAl<sub>2</sub>O<sub>4</sub> and MgAl<sub>2</sub>O<sub>4</sub>) with a face centered cubic (FCC) structure has been shown as an ideal host lattice for transition metal and rare earth ions to generate luminescence with high quantum field.<sup>15–18</sup> By the addition of active Cr<sup>3+</sup> ions with long lifetime into a spinel host, it is promising to realize high efficiency luminescence, and even lasing output.<sup>19,20</sup>

One dimensional nanostructured materials including nanofibers, nanowires and nanotubes have gained much attention due to their unique anisotropic structure, and can be potentially applied as one dimensional waveguides, polarized light resources, lasers, hydrophobicity, energy conversion,

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photocatalysts and sensors in micro/nano-devices.<sup>21-30</sup> As one of the most versatile and effective techniques to prepare nanofibers, electrospinning has been utilized to prepare a variety of polymer and inorganic nanofibers.<sup>29-34</sup> By controlling the precursor solution and electrospun parameters, the morphology, size, microstructure and composition of nanofibers can be conveniently tuned in a wide range. Several typical microstructures (solid, hollow, belt and porous) have been successfully prepared in previous work. 19-25,29-37 For the synthesis of hollow nanofibers by electrospinning, almost all previous work has utilized the coaxial bi-nozzle electrospining equipment.<sup>38–41</sup> It is necessary to use an immiscible oil as the core precursor solution, which is combusted during calcination to form a hollow nanostructure. Thus, the preparation process of hollow nanofibers becomes complex, and the composition of hollow nanofibers is also restricted by the immiscible oil in the core.

Herein, by utilization of a polymer with a low degree of polymerization and controlling the content of polymer and inorganic salts in the precursor solution, spinel hollow nanofibers were synthesized by single-nozzle electrospinning. A 'gaspush' model was proposed to elucidate the formation mechanism of hollow nanofibers. The spectroscopic properties of calcined  $ZnAl_2O_4$ :  $xCr^{3+}$  and  $MgAl_2O_4$ :  $xCr^{3+}$  nanofibers were investigated systematically. By calculation of the crystal field strength of the host, the evolution of photoluminescence (PL) and decay characteristics between  $ZnAl_2O_4$ :  $xCr^{3+}$  and  $MgAl_2O_4$ :  $xCr^{3+}$  and  $MgAl_2O_4$ :  $xCr^{3+}$  nanofibers were well explained.

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## 2. Experimental

# 2.1 Preparation of spinel nanofibers by electrospinning

Chromium-doped spinel (ZnAl<sub>2</sub>O<sub>4</sub>:  $xCr^{3+}$  and MgAl<sub>2</sub>O<sub>4</sub>:  $xCr^{3+}$ ) nanofibers were prepared by electrospinning. Analytical grade Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and Cr(NO<sub>3</sub>)<sub>3</sub>· 9H2O, which were purchased from Sinopharm Chemical Reagent (SCR) Co., Ltd (Shanghai, China), were used as the precursors of Zn, Mg, Al and Cr, respectively. Firstly, 0.86 g Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (or 0.40 g Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) and 2.18 g Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were slowly dissolved in 10 mL mixed solution (ethanol-deionized water (in volume) = 3 : 1). Secondly, a different amount of  $Cr(NO_3)_3 \cdot 9H_2O$ was dissolved in the above solution. After the inorganic salts were completely dissolved into the transparent solution, 3.75 g poly(vinyl pyrrolidone) (PVP, K-30) was dissolved in the above solution with stirring at room temperature. The homogenous solution was used as the precursor solution for electrospinning. The schematic setup of the electrospinning equipment is similar to our previous work.<sup>42,43</sup> The electrospun parameters were optimized as follows: the working distance and voltage was maintained as 12 cm and 20 kV. respectively, and the feeding rate of the solution was fixed at  $1.5 \text{ mL h}^{-1}$ . A metal roller covered with aluminum foil was used as the collector, and the rotation speed was fixed as 200 rpm. After all the precursor solution had been electrospun, the as-prepared nanofibers were taken off and calcined at 1000, 1100 and 1200 °C for 5 h in air with a heating rate of 200  $^{\circ}$ C h<sup>-1</sup>. The designed composition of electrospun nanofibers is  $ZnAl_2O_4$ :  $xCr^{3+}$  (x = 0.005, 0.01, 0.02, 0.03) and MgAl<sub>2</sub>O<sub>4</sub>:  $xCr^{3+}$  (x = 0.01, 0.02, 0.03), respectively. The calcined nanofibers were used for morphology, microstructure and spectroscopic properties characterization.

### 2.2 Characterizations

Structure and crystal phase of electrospun nanofibers was performed using a Rigaku D/MAX X-ray diffractometer (XRD) with Cu K $\alpha$  radiation. Morphology, microstructure and composition of nanofibers was performed on a scanning electron microscope (SEM, Hitachi S4800) equipped with an energy-dispersive X-ray spectrometer (EDS). The high-resolution transmission electron microscopy (HRTEM) images and selected area electron diffraction (SAED) patterns were obtained by a JSM-2010F transmission electron microscope. The diffuse reflectance spectra were recorded by a Perkin-Elmer Lambda 900 wide-range spectrophotometer equipped with an integrating sphere. Photoluminescence (PL) properties and lifetime decay curves were recorded by a FL 920 fluorescence spectrophotometer (Edinburg Instruments). All the measurements were performed at room temperature.

# 3. Results and discussions

# 3.1 Microstructure and morphology

**3.1(a)** Microstructure and morphology of ZnAl<sub>2</sub>O<sub>4</sub>: Cr<sup>3+</sup> electrospun nanofibers. Choosing ZnAl<sub>2</sub>O<sub>4</sub>: 0.01Cr<sup>3+</sup> electrospun nanofibers as the typical sample, we studied the crystalline phase of ZnAl<sub>2</sub>O<sub>4</sub>: *x*Cr<sup>3+</sup> nanofibers calcined at different temperatures. Fig. 1 shows the XRD patterns of ZnAl<sub>2</sub>O<sub>4</sub>: 0.01Cr<sup>3+</sup> electrospun nanofibers calcined at different temperature for 5 h in air. When the as-prepared nanofibers were calcined at 1000 °C, a series of



Fig. 1 XRD patterns of  $ZnAl_2O_4$ : 0.01Cr<sup>3+</sup> electrospun nanofibers calcined at different temperatures for 5 h. (a) 1000 °C, (b) 1200 °C.

obvious diffraction peaks appeared. The intense peaks at  $2\theta = 36.8^{\circ}$  and  $31.2^{\circ}$  are ascribed to the (311) and (220) facet diffraction of FCC ZnAl<sub>2</sub>O<sub>4</sub> phase, and the assignment of other diffraction peaks in the pattern are also labeled in Fig. 1. Almost all of the peaks agree well with the standard cards (JCPDS: 82-1036) of FCC ZnAl<sub>2</sub>O<sub>4</sub> phase, which indicates that the electrospun nanofibers calcined at 1000 °C for 5 h are composed of a pure FCC ZnAl<sub>2</sub>O<sub>4</sub> crystalline phase. When the as-prepared electrospun nanofibers are heated at 1200 °C, the XRD pattern is similar with that heated at 1000 °C. No other peaks ascribed to impurities appear for nanofibers calcined at this temperature. No obvious variation is observed except for the enhancement and sharpness of



**Fig. 2** SEM images of ZnAl<sub>2</sub>O<sub>4</sub>:  $0.01Cr^{3+}$  electrospun nanofibers: (a) as-prepared, (b) calcined at 1200 °C for 5 h, and the scale bar is 10 µm and 2 µm, respectively. The insert shows the amplified SEM image, and the scale bar is 200 nm. (c) EDS spectrum of ZnAl<sub>2</sub>O<sub>4</sub>:  $0.01Cr^{3+}$  nanofibers in Fig. 2(b). The presence of the C peak results from the conductive C films coated on the sample in the course of EDS measurement. (d) TEM image of single ZnAl<sub>2</sub>O<sub>4</sub>:  $0.01Cr^{3+}$  nanofibers in Fig. 2(b), and the scale bar is 200 nm. (e) HRTEM image of ZnAl<sub>2</sub>O<sub>4</sub>:  $0.01Cr^{3+}$  nanofibers in Fig. 2(d), and the scale bar is 5 nm. The insert shows the SAED pattern of single crystal grain.



Fig. 3 Schematic diagram of the growth mechanism of spinel electrospun nanofibers during the calcination in air.

diffraction peaks, which indicates that the crystallinity of nanofibers heated at 1200  $^{\circ}$ C is better than those heated at 1000  $^{\circ}$ C.

Fig. 2 shows the SEM images of the ZnAl<sub>2</sub>O<sub>4</sub>: 0.01Cr<sup>3+</sup> electrospun nanofibers before and after calcination at 1200 °C for 5 h. For the as-prepared nanofibers, super-long nanofibers with an average diameter of  $\sim 800$  nm are obtained by electrospinning in Fig. 2(a). The surface of nanofibers is smooth, and the size distribution of the electrospun nanofibers is relatively homogeneous. After calcination at 1200 °C for 5 h, the average diameter of nanofibers shrinks to  $\sim 600$  nm, and the surface becomes rough. The nanofibers are composed of crystal grains with a size of  $\sim 150$  nm. It is surprising that the nanofibers after calcination are hollow, which can be clearly observed in the insert of Fig. 2(b). Most of the fiber wall consists of single layer crystal grains. Although a number of hollow nanofibers have been prepared by electrospinning, almost all of them were prepared by multi-/bi-nozzle electrospinning. To our knowledge, the synthesis of hollow nanofibers with single-nozzle electrospinning is scarce. The formation mechanism of hollow nanofibers with single walls will be elucidated in the following text. To confirm the elements of calcined nanofibers, an EDS spectrum of ZnAl<sub>2</sub>O<sub>4</sub>: 0.01Cr<sup>3+</sup> nanofibers after calcination at 1200 °C is illustrated in Fig. 2(c). The as-designed elements Zn, Al, O appear in the pattern, and the presence of a C peak results from the conductive C films coated on the sample in the course of EDS measurement. No other impurity is observed in the pattern. Due to the doped content being too low, the peak ascribed to Cr does not obviously appear in the EDS spectrum. Fig. 2(d) shows the TEM image of single calcined ZnAl<sub>2</sub>O<sub>4</sub>: 0.01Cr<sup>3+</sup> nanofiber from Fig. 2(b). It can be seen that the nanofiber consists of crystal grains. The crystal grains are pseudo-spherical, and the average diameter is about 100 nm, which is consistent with the SEM image. The HRTEM image of a single crystal grain is also illustrated in Fig. 2(e). A series of crystal facets with a space of  $\sim 0.466$  nm is observed in the image, which agrees well with the (111) facet diffraction of FCC ZnAl<sub>2</sub>O<sub>4</sub> phase. The SAED pattern of single crystal grain is shown in the insert of Fig. 2(e), which exhibits a typical diffraction pattern of FCC syngony. Combining the HRTEM image and SAED pattern, it can be deduced that every crystal grain in the nanofibers is a single crystal particle.

To attempt to elucidate the growth mechanism of hollow ZnAl<sub>2</sub>O<sub>4</sub>:  $xCr^{3+}$  nanofibers prepared by single-nozzle electrospinning, a 'gas-push' model is proposed in this work, which is schematically illustrated in Fig. 3. When the as-prepared electrospun nanofibers are calcined at 1200 °C in air, a ZnAl<sub>2</sub>O<sub>4</sub> crystal nucleus firstly forms in the nanofibers. Due to the metal nitrate and low polymerized PVP (K-30, (C<sub>6</sub>H<sub>9</sub>NO)<sub>n</sub>) used in the electrospinning, a large number of  $CO_x$ ,  $NO_x$ , *etc.* gas will be generated during calcination. The release of gas will push the crystal nucleus and nitrate precursors to the outer layer of nanofibers, which results in nanofibers with a loose core and a dense outer layer. An obvious gradient distribution of crystal nucleus and nitrate precursors forms in the section of electrospun nanofibers. If the calcination is proceeding, owing to the crystal growth via Oswald-ripening and precursor ion migration, the crystal nucleus and nitrate precursors will migrate from the inner core to the outer layer with a help of sustaining the 'gas-push' effect. When the calcination is completed, ZnAl<sub>2</sub>O<sub>4</sub> crystal grains will form a ring in the outer layer of nanofibers. Finally, a novel microstructure of hollow nanofibers with single wall crystal



Fig. 4 XRD patterns of MgAl<sub>2</sub>O<sub>4</sub>: 0.01Cr<sup>3+</sup> electrospun nanofibers calcined at different temperature for 5 h. (a) 1000 °C, (b) 1100 °C, (c) 1200 °C.

grains forms through the calcination of as-prepared solid electrospun nanofibers.

3.1(b) Microstructure and morphology of MgAl<sub>2</sub>O<sub>4</sub>:  $Cr^{3+}$ electrospun nanofibers. Fig. 4 shows the XRD patterns of MgAl<sub>2</sub>O<sub>4</sub>: 0.01Cr<sup>3+</sup> electrospun nanofibers calcined at different temperatures for 5 h. When the as-prepared nanofibers were calcined at 1000 °C, the intense peaks at  $2\theta = 18.8^{\circ}$ ,  $31.1^{\circ}$ ,  $36.7^{\circ}$ ,  $44.7^{\circ}$ ,  $59.2^{\circ}$  and  $65.1^{\circ}$  can be ascribed to the (111), (220), (311), (400), (511) and (440) facet diffraction of FCC MgAl<sub>2</sub>O<sub>4</sub> phase (JCPDS: 75-1798). However, besides the diffraction peaks owing to the typical FCC MgAl<sub>2</sub>O<sub>4</sub> phase, several other peaks at  $2\theta$  =  $20.8^{\circ}$ ,  $26.6^{\circ}$  and  $50.1^{\circ}$  due to impurities also appear in the pattern, which indicates that the nanofibers calcined at 1000 °C for 5 h are not a pure FCC MgAl<sub>2</sub>O<sub>4</sub> phase. When the asprepared nanofibers were calcined at 1100 °C, almost all the diffraction peaks are assigned to the FCC MgAl<sub>2</sub>O<sub>4</sub> phase. No other impurity appears in the pattern. After the calcined temperature reaches up 1200 °C, besides the better crystallinity of nanofibers, no obvious change is observed in the pattern. Therefore, it can be deduced that the as-prepared electrospun nanofibers calcined at 1100-1200 °C are composed of a pure FCC MgAl<sub>2</sub>O<sub>4</sub> phase with excellent crystallinity.

Fig. 5 shows SEM and TEM images of  $MgAl_2O_4$  nanofibers calcined at 1200 °C. Due to the similar synthesis process and electrospun parameters, the morphology and size of as-prepared  $MgAl_2O_4$  nanofibers is similar with that of  $ZnAl_2O_4$  nanofibers in Fig. 2(a). After calcination at 1200 °C in air, the nanofibers become rough, and are composed of  $MgAl_2O_4$  crystal grains

with a size of ~100 nm. The calcined nanofibers form a hollow microstructure, which is also probably due to the 'gas-push' effect discussed above. Fig. 5(b) shows the EDS spectrum of the calcined MgAl<sub>2</sub>O<sub>4</sub> nanofibers in Fig. 5(a). The as-designed elements Mg, Al and O are detected in the pattern, and no other impurity is observed. Fig. 5(c) shows the TEM image of single MgAl<sub>2</sub>O<sub>4</sub> nanofiber, and the SAED of the nanofiber is illustrated in the insert. The SAED pattern illustrates a series of bright concentric rings, which is a typical polycrystalline SAED pattern. The diffraction indexes are consistent with those of a FCC MgAl<sub>2</sub>O<sub>4</sub> spinel. A HRTEM image of a single MgAl<sub>2</sub>O<sub>4</sub> crystal grain is illustrated in Fig. 5(d). The image shows a series of facets with a crystal space of ~0.468 nm, which corresponds to the (111) facet diffraction of FCC MgAl<sub>2</sub>O<sub>4</sub> phase. The result confirms the XRD patterns of calcined nanofibers in Fig. 4 again.

It is known that the size and morphology of electrospun nanofibers is greatly affected by the experimental parameters, such as polymer content, working distance, accelerating voltage, feeding rate, *etc.* In this work, nanofibers with thinner sizes were also prepared by tuning the electrospinning parameters. Fig. 6 shows the SEM images of MgAl<sub>2</sub>O<sub>4</sub>:  $0.01Cr^{3+}$  electrospun nanofibers prepared with different experimental parameters. The content of PVP in an electrospun precursor solution is decreased into 0.35 g, while the working distance is enlarged into 15 cm. It can be found that the diameter of nanofibers in Fig. 6(a) is ~ 300 nm, which is much thinner than the nanofibers in Fig. 2(a). After calcination at 1200 °C for 5 h, solid nanofibers with an average size of 80 nm are obtained. Due to the large crystal grain and thin diameter, only one or two crystal grains exist in the section of calcined nanofibers.



**Fig. 5** (a) SEM images of MgAl<sub>2</sub>O<sub>4</sub>:  $0.01Cr^{3+}$  electrospun nanofibers calcined at 1200 °C for 5 h, and the scale bar is 2 µm. (b) EDS spectrum of MgAl<sub>2</sub>O<sub>4</sub>:  $0.01Cr^{3+}$  nanofibers in Fig. 5(a). The presence of C peak results from the conductive C films coated on the sample in the course of EDS measurement. (c) TEM image of MgAl<sub>2</sub>O<sub>4</sub>:  $0.01Cr^{3+}$  nanofibers in Fig. 5(a), and the scale bar is 200 nm. The insert shows the SAED pattern of the nanofiber in Fig. 5(c). (d) HRTEM image of MgAl<sub>2</sub>O<sub>4</sub>:  $0.01Cr^{3+}$  nanofibers in Fig. 5(c), and the scale bar is 5 nm.



Fig. 6 SEM images of MgAl<sub>2</sub>O<sub>4</sub>: 0.01Cr<sup>3+</sup> electrospun nanofibers (PVP = 0.35 g). (a) As-prepared, (b) calcined at 1200 °C for 5 h, and the scale bar is 1  $\mu$ m and 100 nm, respectively.





Fig. 7 The diffuse reflectance spectra of  $ZnAl_2O_4$ :  $xCr^{3+}$  electrospun nanofibers calcined at 1200 °C for 5 h. (1) x = 0.005, (2) x = 0.01, (3) x = 0.02, (4) x = 0.03.

Therefore, it is difficult for the thinner nanofibers to form hollow microstructures after calcination.

#### 3.2 Optical properties

**3.2(a) Optical properties of ZnAl<sub>2</sub>O<sub>4</sub>: Cr<sup>3+</sup> electrospun nanofibers.** Fig. 7 shows the diffuse reflectance spectra of ZnAl<sub>2</sub>O<sub>4</sub>: *x*Cr<sup>3+</sup> electrospun nanofibers calcined at 1200 °C for 5 h. Two obvious broad bands centered at 400 nm and 530 nm are observed in the spectra, which are assigned to the  ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}$  and  ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$  spin-allowed transitions of 3d–3d configuration of Cr<sup>3+</sup> ions. A noticeable splitting ( $\lambda = 420$  nm and  $\lambda = 390$  nm) occurs in the  ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}$  transition, which is due to the slight trigonal distortion of the octahedral site in ZnAl<sub>2</sub>O<sub>4</sub> host.  ${}^{44}$  With the addition of Cr<sup>3+</sup> content, the  ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}$  and  ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$ 



**Fig. 8** PL excitation and emission spectra of  $ZnAl_2O_4$ :  $0.01Cr^{3+}$  electrospun nanofibers calcined at 1200 °C for 5 h. The excitation wavelength in emission spectra is 400 nm and 530 nm, while the monitored wavelength in excitation spectra is 676 nm, 687 nm, 698 nm, 709 nm and 718 nm, respectively.

transitions gradually enhance due to the increase of  $Cr^{3+}$  activator.

Due to the better crystallinity of  $ZnAl_2O_4$ :  $xCr^{3+}$  electrospun nanofibers calcined at 1200 °C for 5 h, the PL properties are superior to those calcined at 1000 °C. Therefore, in the following text, choosing nanofibers calcined at 1200 °C for 5 h as the representative sample, the PL properties of spinel nanofibers are investigated in detail. Fig. 8 illustrates the PL excitation and emission spectra of ZnAl<sub>2</sub>O<sub>4</sub>: 0.01Cr<sup>3+</sup> electrospun nanofibers calcined at 1200 °C for 5 h. When the nanofibers are excited by 400 nm, several intense emission peaks appear between 650 nm and 750 nm. The strongest sharp peak at 687 nm, which is well known as the R-line, is due to the spin-forbidden  ${}^{2}E_{\sigma} \rightarrow {}^{4}A_{2\sigma}$ transition of Cr<sup>3+</sup> ions at ideal octahedral site. The other four emission peaks at 676 nm, 698 nm, 709 nm and 718 nm are assigned to the vibrational sidebands  $(VR_{x})$  of zero-phonon R-line with photon assistance. By monitoring the strongest R-line, the excitation spectra are recorded in Fig. 8. Two broad excitation bands centered at 400 nm and 530 nm are detected in the spectra, which are due to the  ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}$  and  ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$ transitions of Cr<sup>3+</sup> ions, respectively. An obvious splitting is also observed in the  ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}$  transitions. It can be found that the excitation spectra are well consistent with the diffuse reflectance spectra of ZnAl<sub>2</sub>O<sub>4</sub>: xCr<sup>3+</sup> nanofibers in Fig. 7. Therefore, in section 4, the data in excitation spectra of calcined spinel nanofibers are utilized to calculate the crystal field strength. We also use the  ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$  transition at 530 nm to excite the sample, and the PL emission spectrum is shown in Fig. 8. The emission lines are similar to the nanofibers excited at 400 nm, while the emission intensity is remarkably intense, which is due to the larger excitation efficiency by  ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$  transition.

To ascertain the optimal doped concentration of Cr in ZnAl<sub>2</sub>O<sub>4</sub>: xCr<sup>3+</sup> electrospun nanofibers. PL spectra of calcined  $ZnAl_2O_4$ : xCr<sup>3+</sup> nanofibers with different Cr doped concentration are also illustrated in Fig. 9. When the nanofibers are excited by 530 nm, similar characteristic emission lines are observed in the excitation spectra. The emission lines between 625-725 nm change proportionally with different Cr doped concentration, while the emission lines between 725-775 nm increase monotonously with the addition of Cr concentration. When monitoring the R-line at 687 nm, the excitation bands at  ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}$  and  ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$  transitions change proportionally with the variety of Cr doped concentration. The intensity of emission and excitation bands, collected as a function of Cr doped concentration, are shown in Fig. 9(b). It can be found that the optimal doped concentration of Cr in  $ZnAl_2O_4$ :  $xCr^{3+}$ electrospun nanofibers is x = 0.01. When the Cr doped concentration is larger than x = 0.01, the intensity of emission lines will decrease gradually due to the enhanced nonradiative relaxation between Cr<sup>3+</sup> ions in different sites.

Fig. 10 shows the decay curves of ZnAl<sub>2</sub>O<sub>4</sub>: xCr<sup>3+</sup> nanofibers calcined at 1200 °C for 5 h. For decay measurement of different emission lines, calcined ZnAl<sub>2</sub>O<sub>4</sub>: 0.01Cr<sup>3+</sup> nanofibers with optimal emission property are chosen as the representative sample. The decay curves of different emission lines at 676 nm, 687 nm, 698 nm, 709 nm and 718 nm are illustrated in Fig. 10(a), which are almost pure exponential decay. By the single-exponential-fit, the lifetime of R-line is ~23.47 ms, which is a characteristic decay of phosphorescence. The



Fig. 9 (a) PL excitation and emission spectra of  $ZnAl_2O_4$ :  $xCr^{3+}$  electrospun nanofibers calcined at 1200 °C for 5 h. The excitation wavelength in emission spectra is fixed as 530 nm, while the monitored wavelength in excitation spectra is fixed as 687 nm. (1) x = 0.005, (2) x = 0.01, (3) x = 0.02, (4) x = 0.03. (b) The peak intensity of excitation and emission peaks in Fig. 9(a) collected with a function of doped Cr concentration.



**Fig. 10** (a) PL decay curves of ZnAl<sub>2</sub>O<sub>4</sub>: 0.01Cr<sup>3+</sup> electrospun nanofibers calcined at 1200 °C for 5 h. The excitation wavelength is fixed as 530 nm, while the monitored emission wavelength is 676 nm, 687 nm, 698 nm, 709 nm and 718 nm, respectively. (b) PL decay curves of ZnAl<sub>2</sub>O<sub>4</sub>: xCr<sup>3+</sup> electrospun nanofibers calcined at 1200 °C for 5 h. The excitation and monitored emission wavelength is fixed as 530 nm and 687 nm, respectively. (1) x = 0.005, (2) x = 0.01, (3) x = 0.02, (4) x = 0.03.

emission line at 676 nm and 698 nm is about 24.27 ms and 23.86 ms, respectively, which is identical to that of the R-line. For the emission line at 709 nm and 718 nm, which is close to the emission band at 725–775 nm, the lifetime is about 21.57 ms and 17.75 ms, respectively. The similar decay characteristics of the emission lines confirm that the emission lines at 676 nm, 698 nm, 709 nm and 718 nm are due to the vibrational sidebands of zero-phonon R-line. Fig. 10(b) shows the decay curves of the R-line from  $ZnAl_2O_4$ :  $xCr^{3+}$  nanofibers with different Cr doped concentrations. It can be found that a slight deviation occurs in decay curves with the increase of Cr content. Using an approximate single-exponential-fit, the lifetime of the R-line is 23.36 ms, 23.47 ms, 18.84 ms and 9.14 ms for x = 0.005, 0.01, 0.02 and 0.03, respectively, which gradually decreases with the increase of Cr content.

**3.2(b)** Optical properties of MgAl<sub>2</sub>O<sub>4</sub>:  $Cr^{3+}$  electrospun nanofibers. Fig. 11 shows the PL excitation and emission spectra of MgAl<sub>2</sub>O<sub>4</sub>: 0.02Cr<sup>3+</sup> electrospun nanofibers calcined at 1200 °C for 5 h. When the nanofibers are excited at 400 nm and 550 nm, a broad emission band with a sharp line at 688 nm is probed. The sharp emission line at 688 nm is the same as the zero-phonon R-line of ZnAl<sub>2</sub>O<sub>4</sub>:  $xCr^{3+}$  nanofibers, which is also due to the  ${}^{2}E_{g} \rightarrow {}^{4}A_{2g}$  transition of  $Cr^{3+}$  ions. The slight shift towards longer wavelength compared with ZnAl<sub>2</sub>O<sub>4</sub>:  $xCr^{3+}$  nanofibers is probably due to the fluctuation of interaction between  $Cr^{3+}$  ions electronic level and lattice vibrations  ${}^{45}$ . Several obvious shoulders, assigned to the vibrational sidebands of the R-line, are detected at 676 nm, 709 nm and 718 nm, respectively. Comparing with the emission spectra of calcined ZnAl<sub>2</sub>O<sub>4</sub>:  $xCr^{3+}$  nanofibers, the emission band of MgAl<sub>2</sub>O<sub>4</sub>:





Fig. 11 PL excitation and emission spectra of  $MgAl_2O_4$ :  $0.02Cr^{3+}$  electrospun nanofibers calcined at 1200 °C for 5 h. The excitation wavelength in the emission spectra is 400 nm and 550 nm, while the monitored wavelength in the excitation spectra is 676 nm, 688 nm, 709 nm and 718 nm, respectively.

 $xCr^{3+}$  nanofibers shows broadband characteristics, and the splitting of the emission line is not obvious with those of  $ZnAl_2O_4$ :  $xCr^{3+}$  fibers. It is probably due to the difference of the crystal field strength of the spinel host, which will be discussed in detail in section 4. By monitoring the R-line emission at 688 nm, two broad excitation bands centered at 400 nm and 550 nm appear in the excitation spectra, which are also due to the  ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}$  and  ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$  transitions of  $Cr^{3+}$  ions, respectively. Comparing with the excitation spectra of  $ZnAl_2O_4$ :  $xCr^{3+}$  nanofibers in Fig. 8, the excitation band of the  ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$  transition in Fig. 11 shifts to a longer wavelength, while no obvious energy shift is detected for the  ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}$  transition.

Fig. 12 illustrates the excitation and emission spectra of calcined  $MgAl_2O_4$ :  $xCr^{3+}$  nanofibers with different Cr doping



**Fig. 12** PL excitation and emission spectra of MgAl<sub>2</sub>O<sub>4</sub>: xCr<sup>3+</sup> electrospun nanofibers calcined at 1200 °C for 5 h. The excitation wavelength in the emission spectra is fixed at 550 nm, while the monitored wavelength in the excitation spectra is fixed as 688 nm. (1) x = 0.01, (2) x = 0.02, (3) x = 0.03.

concentrations. For the emission spectra with a 550 nm excitation, the emission band at 725–800 nm increases monotonously with the increase of Cr content, which is similar with the emission spectra of ZnAl<sub>2</sub>O<sub>4</sub>:  $xCr^{3+}$  nanofibers in Fig. 9(a). For the excitation spectra monitoring the R-line at 688 nm, the ratio of the excitation band intensity of 550 nm to 400 nm slightly increases with the increase of Cr content. From the excitation and emission spectra of MgAl<sub>2</sub>O<sub>4</sub>:  $xCr^{3+}$  nanofibers in Fig. 12, it can be deduced that the optimal doped concentration of Cr is x = 0.02 in MgAl<sub>2</sub>O<sub>4</sub>:  $xCr^{3+}$  electrospun nanofibers.

The decay curves of MgAl<sub>2</sub>O<sub>4</sub>: xCr<sup>3+</sup> electrospun nanofibers are shown in Fig. 13. Choosing MgAl<sub>2</sub>O<sub>4</sub>: 0.02Cr<sup>3+</sup> nanofibers as a representative sample, the decay curves of different emission lines are illustrated in Fig. 13(a). It can be found that the decay characteristic is different from those of ZnAl<sub>2</sub>O<sub>4</sub>: 0.01Cr<sup>3+</sup> nanofibers, and a slight deviation occurs in decay curves. If we use a single-exponential-fit to evaluate the lifetime of emission lines, the lifetime of 688 nm, 709 nm and 718 nm emission lines is about 8.75 ms, 6.02 ms and 5.50 ms, respectively. The lifetime of Cr<sup>3+</sup> doped MgAl<sub>2</sub>O<sub>4</sub> nanofibers is much shorter than that in ZnAl<sub>2</sub>O<sub>4</sub> nanofibers. From the R-line to low energy emission lines, the lifetime decreases gradually, which is similar with that of ZnAl<sub>2</sub>O<sub>4</sub>:  $xCr^{3+}$  nanofibers in Fig. 10(a). Under a 550 nm excitation, the decay curves of R-line in MgAl<sub>2</sub>O<sub>4</sub>: xCr<sup>3+</sup> nanofibers with different Cr doped concentration is also illustrated in Fig. 13(b). The decay curves also slightly deviate from single-exponential process. By using single-exponential-fit, the lifetime of R-line decreases from 10.78 ms to 8.75 ms and 6.33 ms when the Cr doped concentration increases from 0.01 to 0.02 and 0.03.

#### 3.3 Discussion

It is known that luminescence properties of  $Cr^{3+}$  ions depend strongly on their coordination, crystal field, lattice imperfections, *etc.* From the Tanabe–Sugano diagram, it can be deduced that the lowest excited state (<sup>2</sup>E<sub>g</sub> or <sup>4</sup>T<sub>2g</sub>) depends mainly on the crystal field strength,  $D_q/B$ .<sup>46</sup> When  $Cr^{3+}$  ions lie at sites with strong or intermediate crystal field, *i.e.*  $D_q/B \ge 2.3$ , the lowest excited state is the <sup>2</sup>E<sub>g</sub> level, which will be responsible for the narrow band phosphorescence with a characteristic lifetime of tens of ms. In the case where  $Cr^{3+}$  ions lie at sites with weak crystal field, *i.e.*  $D_q/B \le$ 2.3, the lowest excited state will be the <sup>4</sup>T<sub>2g</sub> level, which will be responsible for the broad band fluorescence with a characteristic lifetime of tens of µs. Therefore, before discussing the noticeable difference between the luminescence properties of ZnAl<sub>2</sub>O<sub>4</sub>:  $xCr^{3+}$ and MgAl<sub>2</sub>O<sub>4</sub>:  $xCr^{3+}$  nanofibers, it should elucidate the crystal structure of spinel.

The so-called normal spinel is described by AB<sub>2</sub>O<sub>4</sub>, where A denotes divalent anion, such as  $Zn^{2+}$ ,  $Mg^{2+}$ , *etc.* B denotes trivalent anion, such as Al<sup>3+</sup>, Ga<sup>3+</sup>, *etc.* As the crystal structure in Fig. 14(a), the spinel structure is a FCC phase with a space group of *Fd-3m.* In the normal spinel host lattice,  $A^{2+}$  (Zn<sup>2+</sup>,  $Mg^{2+}$ , *etc.*) ions occupy tetrahedral sites ( $T_d$  symmetry) and B<sup>3+</sup> (Al<sup>3+</sup>, Ga<sup>3+</sup>, *etc.*) ions occupy octahedral sites ( $D_{3d}$  symmetry), as shown in Fig. 14(b) and (c), respectively.<sup>47</sup> When trivalent Cr<sup>3+</sup> ions are doped into a spinel host, due to the  $3d^3$  electron configuration of Cr<sup>3+</sup> ions, the crystal field stabilization energy of Cr<sup>3+</sup> ions in octahedral sites is almost three times greater than



**Fig. 13** (a) PL decay curves of MgAl<sub>2</sub>O<sub>4</sub>: 0.02Cr<sup>3+</sup> electrospun nanofibers calcined at 1200 °C for 5 h. The excitation wavelength is fixed at 550 nm, while the monitored emission wavelength is 688 nm, 709 nm and 718 nm, respectively. (b) PL decay curves of MgAl<sub>2</sub>O<sub>4</sub>: xCr<sup>3+</sup> electrospun nanofibers calcined at 1200 °C for 5 h. The excitation and monitored emission wavelength is fixed at 550 nm and 688 nm, respectively. (1) x = 0.01, (2) x = 0.02, (3) x = 0.03.



Fig. 14 (a) The crystal structure schematic diagram of  $ZnAl_2O_4$  (MgAl<sub>2</sub>O<sub>4</sub>) spinel. (b) Tetrahedral sites occupied by  $Zn^{2+}$  or  $Mg^{2+}$  ions (purple tetrahedral). (c) Octahedral sites occupied by  $Al^{3+}$  ions (pink octahedral).

in tetrahedral sites. So  $Cr^{3+}$  ions lie preferentially in octahedral sites to replace  $B^{3+}$  (Al<sup>3+</sup>, Ga<sup>3+</sup>, *etc.*) ions.<sup>44</sup>

From the XRD results in Fig. 1 and Fig. 4 and the crystallographic ICSD data, the lattice constants and bond length can be estimated as follows. For the  $ZnAl_2O_4$ :  $0.01Cr^{3+}$  nanofibers calcined at 1200 °C for 5 h, the lattice constants are a = b = c = 8.088 Å, while the bond length (*R*) of Mg–O bond and Al–O bond is about 1.967 Å and 1.906 Å, respectively (data from ICSD #94156). For the MgAl<sub>2</sub>O<sub>4</sub>:  $0.01Cr^{3+}$  nanofibers calcined at 1200 °C for 5 h, the lattice constants are a = b = c = 8.114 Å, while the bond length (*R*) of Mg–O bond and Al–O bond is about 1.933 Å and 1.932 Å, respectively (Data from ICSD #31376). From previous work,<sup>48,49</sup> it is known that crystal field strength,  $D_q$  is inversely proportional to the quintic of the bond length, *R*:

$$D_q \propto 1/R^5 \tag{1}$$

The shorter bond length means a stronger crystal field strength. Because  $Cr^{3+}$  ions occupy the octahedral sites of  $Al^{3+}$  ions, the bond length of Al–O bond can be utilized to estimate the crystal field strength around  $Cr^{3+}$  ions. Due to the bond length of Al–O bond in MgAl<sub>2</sub>O<sub>4</sub>: 0.01Cr<sup>3+</sup> being larger than in ZnAl<sub>2</sub>O<sub>4</sub>: 0.01Cr<sup>3+</sup> nanofibers, it can be deduced that the crystal field strength around  $Cr^{3+}$  ions in MgAl<sub>2</sub>O<sub>4</sub>: 0.01Cr<sup>3+</sup> is weaker than that in ZnAl<sub>2</sub>O<sub>4</sub>: 0.01Cr<sup>3+</sup> nanofibers. The relatively precise crystal field strength parameters can be estimated by spectroscopic data as follows:<sup>50,51</sup>

$$10D_q = v_2 \tag{2}$$

$$B = (v_1^2 + 2v_2^2 - 3v_1v_2)/(15v_1 - 27v_2)$$
(3)

where  $v_1$  and  $v_2$  is the energy corresponding to  ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}$  and  ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$  transitions of  $Cr^{3+}$  ions, respectively. For ZnAl<sub>2</sub>O<sub>4</sub>:  $xCr^{3+}$  nanofibers,  $v_1 = 25\ 000\ cm^{-1}$  and  $v_2 = 18\ 868\ cm^{-1}$ , then  $D_q$  and *B* are estimated to be 1887 cm<sup>-1</sup> and 581 cm<sup>-1</sup>, respectively. While for MgAl<sub>2</sub>O<sub>4</sub>:  $xCr^{3+}$  nanofibers,  $v_1 = 25\ 000\ cm^{-1}$  and  $v_2 = 18\ 182\ cm^{-1}$ , then  $D_q$  and *B* is estimated to be 1818 cm<sup>-1</sup> and 668 cm<sup>-1</sup>, respectively. Therefore, the crystal field strength parameter of  $D_q/B$  is calculated to be 3.25 and 2.72 for ZnAl<sub>2</sub>O<sub>4</sub>:  $xCr^{3+}$  and MgAl<sub>2</sub>O<sub>4</sub>:  $xCr^{3+}$  nanofibers, respectively.

Based on the calculation of crystal field strength above, the PL excitation, emission and decay properties will be discussed successively in the following text.

When  $Cr^{3+}$  ions occupy the octahedral sites, the influence of the octahedral crystal field will split the ground term <sup>4</sup>F into the ground level <sup>4</sup>A<sub>2g</sub> and two excited levels <sup>4</sup>T<sub>1g</sub> and <sup>4</sup>T<sub>2g</sub>. The ground level and the first excited level result from  $t_{2g}^3$  configuration, while the second excited level <sup>4</sup>T<sub>2g</sub> is a  $t_{2g}^2e_g$  configuration. Because the  $e_g$  orbital is along the octahedral axis, the excited level <sup>4</sup>T<sub>2g</sub> depends strongly on the crystal field strength. Therefore, compared with the excitation spectra of ZnAl<sub>2</sub>O<sub>4</sub>:  $xCr^{3+}$  nanofibers, the excitation

band of  ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$  transition shifts from 530 nm to 550 nm for MgAl<sub>2</sub>O<sub>4</sub>:  $xCr^{3+}$  nanofibers due to the weaker crystal field strength.

It is known that a large number of  $Cr^{3+}$  sites exist in the spinel host. When the ZnAl<sub>2</sub>O<sub>4</sub>: xCr<sup>3+</sup> and MgAl<sub>2</sub>O<sub>4</sub>: xCr<sup>3+</sup> nanofibers are excited by  ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}$  and  ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$  transitions, the emission lines at 675-725 nm in the PL emission spectra are due to the emission of Cr<sup>3+</sup> ions lying at strong crystal field strength sites, while the emission band at 725-800 nm is due to the emission of Cr<sup>3+</sup> ions lying at weak crystal field strength sites.<sup>52</sup> Due to the smaller crystal field strength,  $D_q/B$  for MgAl<sub>2</sub>O<sub>4</sub>: xCr<sup>3+</sup> nanofibers, which is close to the critical value  $(D_a/B = 2.3)$ , it can be deduced that Cr<sup>3+</sup> ions lying at weak crystal field in MgAl<sub>2</sub>O<sub>4</sub>:  $xCr^{3+}$  nanofibers are more than those in ZnAl<sub>2</sub>O<sub>4</sub>:  $xCr^{3+}$ nanofibers. This will result in an optimal doping concentration of  $Cr^{3+}$  ions as the R-line emission in MgAl<sub>2</sub>O<sub>4</sub>:  $xCr^{3+}$  nanofibers (x = 0.02) is larger than ZnAl<sub>2</sub>O<sub>4</sub>: xCr<sup>3+</sup> nanofibers (x = 0.01). The crystal field around Cr<sup>3+</sup> ions in MgAl<sub>2</sub>O<sub>4</sub>: xCr<sup>3+</sup> nanofibers is almost a continuous distribution, which can be confirmed by the broadening of emission lines and the increase of background in emission spectra of MgAl<sub>2</sub>O<sub>4</sub>: xCr<sup>3+</sup> nanofibers. With the increase of Cr doped concentration in spinel nanofibers, the lattice disorder of the spinel host will increase. More Cr<sup>3+</sup> ions will occupy the distorted octahedral sites with weak crystal field, which will result in the monotonous increase of the emission band at 725-800 nm with the addition of  $Cr^{3+}$  concentration.

As shown in Fig. 10(a) and Fig. 13(a), due to the contribution from 725-800 nm the emission of Cr<sup>3+</sup> ions at weak crystal field increases from 676 nm to 718 nm, the lifetime of emission lines from 676 nm to 718 nm slightly shortens, especially for the emission at longer wavelengths. Compared with the decay curves of ZnAl<sub>2</sub>O<sub>4</sub>: xCr<sup>3+</sup> nanofibers, the lifetime of Cr<sup>3+</sup> ions is much shorter and the decay curves deviate from a single-exponential process in MgAl<sub>2</sub>O<sub>4</sub>:  $xCr^{3+}$  nanofibers. It is also due to the larger contribution from the emission of Cr<sup>3+</sup> ions at weak crystal field, which results in a double phosphorescence and fluorescence behavior in MgAl<sub>2</sub>O<sub>4</sub>:  $xCr^{3+}$  nanofibers. When the concentration of Cr<sup>3+</sup> ions in spinel nanofibers increase, due to a large number of Cr<sup>3+</sup> ions occupying the weak crystal field sites, the proportion of Cr<sup>3+</sup> ions with fluorescence behavior increases. Therefore, with the increase of Cr concentration in spinel nanofibers, the lifetime shortens remarkably and the deviation from single-exponential process becomes more clear.

#### 4. Conclusion

By using a single-nozzle electrospinning technique,  $ZnAl_2O_4$ :  $xCr^{3+}$  and  $MgAl_2O_4$ :  $xCr^{3+}$  hollow nanofibers were synthesized after calcination in air. SEM and TEM results indicate that the calcined nanofibers are hollow microstructures consisting of single layer crystal grains. A 'gas-push' model is proposed to elucidate the formation mechanism of hollow nanofibers. Under an excitation at 430 nm or 530 nm for  $ZnAl_2O_4$ :  $xCr^{3+}$  nanofibers, a sharp R-line emission at 687 nm with several vibrational sidebands appears. For  $MgAl_2O_4$ :  $xCr^{3+}$  nanofibers, the broadening of emission lines and the increase of background is observed. The lifetime of  $Cr^{3+}$  ions in  $ZnAl_2O_4$ :  $xCr^{3+}$  nanofibers is about 10–25 ms, while it is about 5–10 ms of  $MgAl_2O_4$ :  $xCr^{3+}$  nanofibers. And in both spinel nanofibers, the lifetime becomes

shorter when the monitored emission peak shifts to longer wavelength. Based on the energy of  ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}$  and  ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$ transitions of Cr<sup>3+</sup> ions, the crystal field strength parameter,  $D_q/B$  is estimated to be 3.25 and 2.72 for ZnAl<sub>2</sub>O<sub>4</sub>: xCr<sup>3+</sup> and MgAl<sub>2</sub>O<sub>4</sub>: xCr<sup>3+</sup> nanofibers, respectively. The difference of  $D_q/B$ value gives a good explanation of the spectroscopic and decay evolution between ZnAl<sub>2</sub>O<sub>4</sub>: xCr<sup>3+</sup> and MgAl<sub>2</sub>O<sub>4</sub>: xCr<sup>3+</sup> nanofibers. The spinel hollow nanofibers with high efficiency and tunable bandwidth luminescence are expected to be applied as waveguides, sensors, displays and lighting in micro/nanodevices.

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#### References

- 1 Y. Nakayama, P. J. Pauzauskie, A. Radenovic, R. M. Onorato, R. J. Saykally, J. Liphardt and P. D. Yang, *Nature*, 2007, **447**, 1098.
- 2 F. Wang, Y. Han, C. S. Lim, Y. H. Lu, J. Wang, J. Xu, H. Y. Chen, C. Zhang, M. H. Hong and X. G. Liu, *Nature*, 2010, **463**, 1061.
- 3 Z. H. Nie, A. Petukhova and E. Kumacheva, *Nat. Nanotechnol.*, 2010, **5**, 15.
- 4 F. Zhang, Y. Wang, T. Yu, F. Q. Zhang, Y. F. Shi, S. H. Xie, Y. G. Li, L. Xu, B. Tu and D. Y. Zhao, *Angew. Chem., Int. Ed.*, 2007, 46, 7976.
- 5 C. L. Yan, A. Dadvand, F. Rosei and D. F. Perepichka, J. Am. Chem. Soc., 2010, 132, 8868.
- 6 D. Q. Chen, Y. L. Yu, F. Huang, P. Huang, A. P. Yang and Y. S. Wang, J. Am. Chem. Soc., 2010, 132, 9976.
- 7 Y. S. Liu, D. T. Tu, H. M. Zhu, R. F. Li, W. Q. Luo and X. Y. Chen, *Adv. Mater.*, 2010, **22**, 3266.
- 8 J. Liu and Y. D. Li, Adv. Mater., 2007, 19, 1118.
- 9 C. L. Yan, L. Nikolova, A. Dadvand, C. Harnagea, A. Sarkissian, D. F. Perepichka, D. F. Xue and F. Rosei, *Adv. Mater.*, 2010, 22, 1741.
- 10 J. Wu and J. L. Coffer, Chem. Mater., 2007, 19, 6266.
- 11 H. W. Song, H. Q. Yu, G. H. Pan, X. Bai, B. Dong, X. T. Zhang and S. K. Hark, *Chem. Mater.*, 2008, **20**, 4762.
- 12 Z. Y. Hou, C. X. Li, J. Yang, H. Z. Lian, P. P. Yang, R. T. Chai, Z. Y. Chen and J. Lin, J. Mater. Chem., 2009, 19, 2737.
- 13 Z. Y. Hou, P. P. Yang, C. X. Li, L. L. Wang, H. Z. Lian, Z. W. Quan and J. Lin, *Chem. Mater.*, 2008, **20**, 6686.
- 14 G. P. Dong, X. D. Xiao, Y. Z. Chi, B. Qian, X. F. Liu, Z. J. Ma, E. Wu, H. P. Zeng, D. P. Chen and J. R. Qiu, *J. Mater. Chem.*, 2010, **20**, 1587.
- 15 K. Izumi, S. Miyazaki, S. Yoshida, T. Mizokawa and E. Hanamura, *Phys. Rev. B*, 2007, **76**, 075111.
- 16 A. Jouini, A. Yoshikawa, A. Brenier, T. Fukuda and G. Boulon, *Phys. Status Solidi C*, 2007, 4, 1380.
- 17 K. Y. Jung, H. W. Lee and H. K. Jung, Chem. Mater., 2006, 18, 2249.
- 18 H. Matsui, C. N. Xu and H. Tateyama, Appl. Phys. Lett., 2001, 78, 1068.
- 19 S. Kück, Appl. Phys. B, 2001, 72, 515.
- 20 W. Z. Yan, F. Liu, Y. Y. Lu, X. J. Wang, M. Yin and Z. W. Pan, Opt. Express, 2010, 18, 20215.
- 21 F. D. Benedetto, A. Camposeo, S. Pagliara, E. Mele, L. Persano, R. Stabile, R. Cingolani and D. Pisignano, *Nat. Nanotechnol.*, 2008, 3, 614.

- 22 Y. Xiao, C. Meng, P. Wang, Y. Ye, H. K. Yu, S. S. Wang, F. X. Gu, L. Dai and L. M. Tong, *Nano Lett.*, 2011, **11**, 1122.
- 23 H. Wu, Y. Sun, D. D. Lin, R. Zhang, C. Zhang and W. Pan, Adv. Mater., 2009, 21, 227.
- 24 J. M. Moran-Mirabal, J. D. Slinker, J. A. DeFranco, S. S. Verbridge, R. Ilic, S. Flores-Torres, H. Abruna, G. G. Malliaras and H. G. Craighead, *Nano Lett.*, 2007, 7, 458.
- 25 G. P. Dong, X. D. Xiao, Y. Z. Chi, B. Qian, X. F. Liu, Z. J. Ma, S. Ye, E. Wu, H. P. Zeng, D. P. Chen and J. R. Qiu, *J. Phys. Chem. C*, 2009, **113**, 9595.
- 26 X. F. Duan, Y. Huang, R. Agarwal and C. M. Lieber, *Nature*, 2003, 421, 241.
- 27 A. I. Hochbaum and P. D. Yang, Chem. Rev., 2010, 110, 527.
- 28 Z. R. Tang, Y. H. Zhang and Y. J. Xu, RSC Adv., 2011, 1, 1772.
- 29 M. L. Chen, M. D. Dong, R. Havelund, V. R. Regina, R. L. Meyer, F. Besenbacher and P. Kingshott, *Chem. Mater.*, 2010, 22, 4214.
- 30 M. L. Chen and F. Besenbacher, ACS Nano, 2011, 5, 1549.
- 31 J. Song, M. L. Chen, M. Buster Olesen, C. X. Wang, R. Havelund, Q. Li, E. Q. Xie, R. Yang, P. Bøggild, C. Wang, F. Besenbacher and M. D. Dong, *Nanoscale*, 2011, 3, 4966.
- 32 X. F. Lu, C. Wang and Y. Wei, Small, 2009, 5, 2349.
- 33 A. Greiner and J. H. Wendorff, Angew. Chem., Int. Ed., 2007, 46, 5670.
- 34 D. Li and Y. N. Xia, Adv. Mater., 2004, 16, 1151.
- 35 D. Li and Y. N. Xia, Nano Lett., 2004, 4, 933.
- 36 M. Bognitzki, W. Czado, T. Frese, A. Schaper, M. Hellwig, M. Steinhart, A. Greiner and J. H. Wendorff, *Adv. Mater.*, 2001, 13, 70.
- 37 S. Koombhongse, W. X. Liu and D. H. Reneker, J. Polym. Sci., Part B: Polym. Phys., 2001, 39, 2598.

- 38 W. Li, C. Y. Cao, C. Q. Chen, Y. Zhao, W. G. Song and L. Jiang, *Chem. Commun.*, 2011, **47**, 3619.
- 39 T. Y. Zhao, Z. Y. Liu, K. Nakata, S. Nishimoto, T. Murakami, Y. Zhao, L. Jiang and A. Fujishima, J. Mater. Chem., 2010, 20, 5095.
- 40 J. C. Di, H. Y. Chen, X. F. Wang, Y. Zhao, L. Jiang, J. H. Yu and R. R. Xu, *Chem. Mater.*, 2008, **20**, 3543.
- 41 D. Li, J. T. McCann and Y. N. Xia, Small, 2005, 1, 83.
- 42 G. P. Dong, X. D. Xiao, L. L. Zhang, Z. J. Ma, X. Bao, M. Y. Peng, Q. Y. Zhang and J. R. Qiu, J. Mater. Chem., 2011, 21, 2194.
- 43 G. P. Dong, X. F. Liu, X. D. Xiao, B. Qian, J. Ruan, S. Ye, H. C. Yang, D. P. Chen and J. R. Qiu, *Nanotechnology*, 2009, **20**, 055707.
- 44 P. J. Deren, M. Malinowski and W. Strqk, J. Lumin., 1996, 68, 91.
- 45 V. C. Costa, F. S. Lameiras, M. V. B. Pinheiro, D. F. Sousa, L. A. O. Nunes, Y. R. Shen and K. L. Bray, J. Non-Cryst. Solids, 2000, 273, 209.
- 46 S. Sugano, Y. Tanabe and H. Kamimura, *Multiplets of Transition-Metal Ions in Crystals*, Academic Press, New York, 1970.
- 47 S. B. Berger, J. Appl. Phys., 1965, 36, 1048.
- 48 B. Henderson and G. G. Imbush, Optical Spectroscopy of Inorganic Solids, Clarendon, Oxford, 1989.
- 49 S. Ye, Z. S. Liu, X. T. Wang, J. G. Wang, L. X. Wang and X. P. Jing, J. Lumin., 2009, 129, 50.
- 50 V. Singh, R. P. S. Chakradhar, J. L. Rao and D. K. Kim, J. Lumin., 2009, **129**, 130.
- 51 W. W. Zhang, J. Y. Zhang, Z. Y. Chen, T. M. Wang and S. K. Zheng, J. Lumin., 2010, 130, 1738.
- 52 K. E. Lipinska-Kalita, P. E. Kalita, D. M. Krol, R. J. Hemley, C. L. Gobin and Y. Ohki, J. Non-Cryst. Solids, 2006, 352, 524.