A soluble salt-assisted facile synthetic route to semiconducting GaN nanoparticles†

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By using the soluble salt as the dispersant, a facile synthetic route has been developed to prepare GaN nanoparticle powders on a large scale and in a high yield of 95.8% through the direct nitridation of Ga–Na_2SO_4 mixture at 700 °C and followed by washing with water. This preparation method is also applicable to some other low-melting-point-metal oxides. The simple preparation procedure and the range of potential applications of the products made this work both scientifically and technologically interesting.

1. Introduction

Inorganic semiconducting nanoparticles (NPs) have potential applications that result from unusual electronic, optical, and magnetic properties hardly embodied in their bulk counterparts.[1] As one of the most important wide band-gap semiconductors, gallium nitride (GaN) has attracted much attention since the successful fabrication of high-efficiency blue light-emitting diodes.[2,3] One might expect that GaN powder had better be made simply and economically by the direct nitridation of metallic Ga with ammonia or nitrogen at high temperatures, similar to the large-scale preparation of nano-scaled AlN powder, which would not introduce any other impurities but Ga and N elements during the preparation process.[4] However, metallic Ga exists in the form of large droplets above 30 °C because of its high surface tension, and nitrogen atoms are sparingly soluble in these droplets even at temperatures above 1000 °C.[5,6] Therefore, few papers have reported the large-scale synthesis of GaN NPs by the direct nitridation of metallic Ga.[6] In contrast, there have been numerous reports of the deposition of GaN nanowires on substrates by the nitridation of gaseous metallic Ga at high temperatures.[7] In order to access this valuable material on a large scale, some expensive, air-sensitive and even rather toxic gallium-based precursors, inevitably combining hazardous manipulations, have been studied. For example, $GaCl_3$ was often used to react with urea or other complex nitrogen resources to form large Ga-based organometallic molecules, thereby through the decomposition of the as-synthesized large Ga-based molecules at low temperature the needed GaN NPs were obtained on a large scale.[8–11] Ga_2O_3 powders and carbon–nitrogen-containing precursors were also used to obtain GaN nanoparticles via a carbothermal reduction process, which is difficult to scale-up due to the high pressures needed.[12] Those routes to GaN NPs would inevitably introduce the residual carbon, which is very difficult to remove from the products. Although gallium halides and alkali nitrides can undergo a solid-state metathesis reaction to prepare GaN on a larger scale, temperatures as high as 1100 °C are reached in these very exothermic reactions, which can lead to the decomposition of GaN.[13,14] This problem is also relevant to Paine and Mokaya's reports of the nitridation of Ga_2O_3 or $GaCl_3$ powders for the synthesis of GaN powder.[15,16] The direct nitridation of metallic Ga at lower temperatures would be very desirable for the large-scale synthesis of GaN, because it would not introduce impurity elements and would not involve temperatures where GaN is unstable.

In our previous reports, we found that the vapour pressure of metallic Ga could be greatly increased by dispersing it as tiny, uniform droplets onto an inert salt. The synthesis temperature of GaN nanowires could thus be lowered substantially to 650 °C.[17,18] Ga droplets could be well dispersed on CaF_2 even at 650 °C and completely nitrified into GaN powder, which was however then inseparable from the insoluble CaF_2 powder. In this study, the insoluble CaF_2 support was replaced with a soluble salt (Na_2SO_4), and GaN nanoparticles were obtained in high yield after simply washing with distilled water.

2. Experimental

In a typical run, 1 g of metallic Ga and 10 g of Na_2SO_4 powder were combined in a mortar and milled for 30 min by manual operation at 35 °C. Then the mixture was transferred into a quartz tube and nitrified at 700 °C for 3 h. The nitriding procedure in mixed NH_3/N_2 is similar to that described in our previous reports.[17,18] The nitriding mixture was then washed with distilled water several times until the SO_4^{2-} ions could not be detected in the filtrate. Finally, the filtered product was dried in an oven at 90 °C for 3 h and 1.15 g of pale yellow powder was obtained. The yield of GaN was 95.8%, based on the amount of Ga used. The small loss of GaN is probably from the washing and filtering process. The product was characterized by X-ray diffraction (XRD; Philips X'pert Pro diffractometer), micro-Raman spectroscopy (excited with an Ar⁺ laser at 488 nm), scanning electron microscopy (SEM; JEOL JSM-6300) equipped with energy-dispersive X-ray analysis (EDX), and high-resolution transmission electron microscopy (HRTEM; JEM-40001X).

3. Results and discussion

The XRD pattern and Raman spectrum of the product unambiguously identify the hexagonal GaN phase as shown in Fig. 1. The

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† Electronic supplementary information (ESI) available: XRD patterns and TEM images of Ga_2O_3, ZnO, In_2O_3 and SnO_2 nanoparticles. See DOI: 10.1039/b923920k
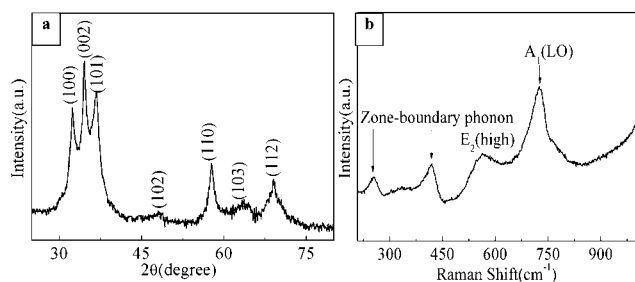
Fig. 1   (a) XRD pattern and (b) Raman spectrum of the GaN NPs.

broadened peaks from the XRD and Raman patterns also indicate that the grain size is on the nanometre scale. The low-intensity ratio of $I(E_2(high))/I(A_1(LO))$ reveals high crystallinity of the GaN NPs.[19] According to the Scherrer equation ($D = K\lambda/\beta\cos\theta$), the mean diameter is about 7.6 nm here taking $\theta = 57.72°$ for example. The absence of other peaks demonstrates the high purity of the nanoparticles product.

Fig. 2 shows a typical SEM image of the GaN product, revealing an aggregation of nanoparticles. The inset is the corresponding EDX pattern, which indicates the presence of the elements Ga, N, and O. The O peak is due to the unavoidable surface oxidation of the dangling bonds in non-layered compounds.[20] The absences of Na and S signals further demonstrates the high purity of the product, and is consistent with the XRD and Raman results.

The TEM images (Fig. 3a and b) show an agglomerate of many GaN nanoparticles; in particular the dark-field TEM image clearly indicates the sizes of GaN nanoparticles are in the range of several nanometres. This morphologic observation is close to the calculation value from Scherrer equation. The HRTEM images (Fig. 3c) did not show distinct particles with well defined crystalline boundaries, which might result from polycrystalline material. The selected area electron diffraction (SAED) pattern (inset in a) of an aggregate gives a set of weak diffraction circles indicating that it is polycrystalline. The pattern could be well indexed to hexagonal GaN in agreement with the XRD and Raman results. The spacing of 2.57 Å between adjacent fringes corresponds to the d-spacing of (001) planes in hexagonal GaN.

Photoluminescence (PL) measurements of the GaN nanopowder obtained in this work were carried out using a fluorescence spectrophotometer (Perkin Element LS50-B) with a Xe lamp and the results
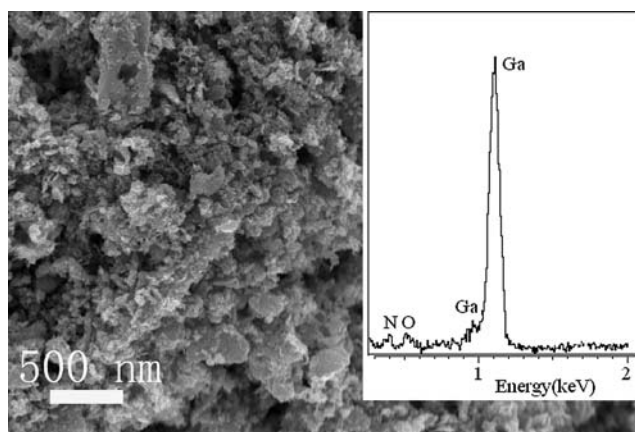

Fig. 2   SEM image of the GaN NPs. Inset is the EDX pattern.
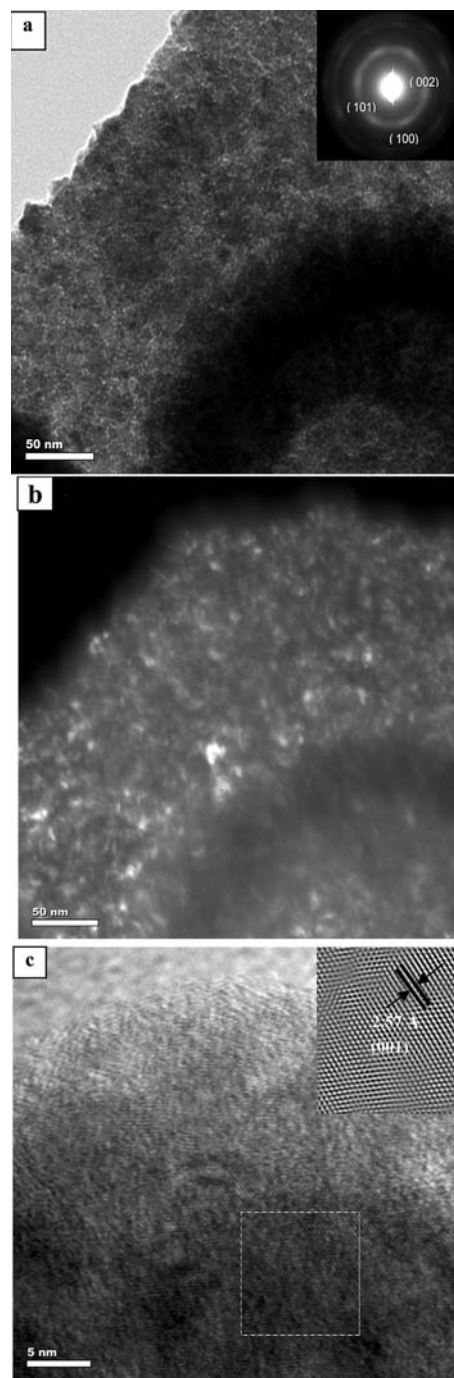
Fig. 3   TEM image (a) and dark-field TEM image (b) and HRTEM image (c) of the GaN NPs. Insets are the corresponding SAED pattern and the Fourier transform, respectively. The scale bar is 50 nm for TEM or 5 nm for HTREM.

are shown in Fig. 4. The broad emission band from 350 nm to 550 nm might be ascribed to trap states[11] and the band edge emissions of both the hexagonal-structured and the cubic-phase structured GaN,[21] which was not detected by XRD and SAED. However, the mechanism of these emissions is not clear yet, and is worth exploring further.

The successful preparation of GaN NPs on a large scale as described above can be attributed to the dispersion of Ga on Na_2SO_4.
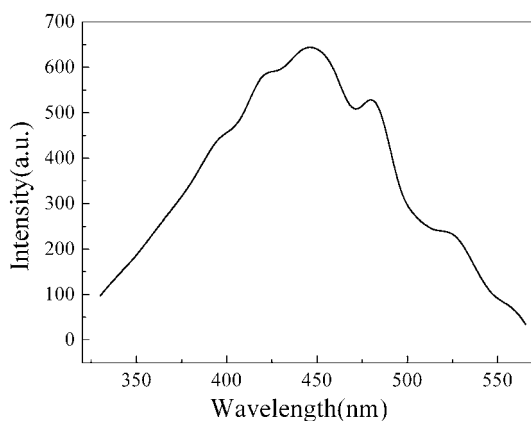
Fig. 4 PL emission spectra of GaN nanopowders at room temperature with an excitation wavelength of 300 nm.

In the absence of Na_2SO_4, the direct nitridation of metallic Ga did not produce detectable amounts of GaN powder even at 1000 °C.[5,6] The optimal weight ratio of Ga and Na_2SO_4 is 1 : 10, which is adequate to obtain high dispersion of Ga droplets onto Na_2SO_4 powder. It should be noted that the Na_2SO_4 in filtrate can be reused several times after the water is evaporated. Finally, the nitriding temperature should not exceed 750 °C since Na_2SO_4 will decompose above 800 °C.

Using this soluble salt-assisted route, Ga_2O_3 NPs were also obtained on a large scale when NH_3 was replaced by air. Moreover, other low-melting-point soft metallic oxides, such as ZnO, In_2O_3 and SnO_2 could be prepared as NPs by ball-milling the mixture of metal and Na_2SO_4 powder followed by the oxidation in air and washing with distilled water (see ESI).†

Our attempts to prepare AlN and InN NPs by this new route have so far been unsuccessful. It is however possible that ball-milling Al or In powder and Na_2SO_4 in Ar and the followed nitridation will yield AlN or InN nanoparticles. Compared with previous reports,[22,23] this new route is especially simple, economical and potentially useful.

4. Conclusion

In summary, by using the soluble salt as the dispersant, a facile synthetic route has been developed to prepare GaN nanoparticles on a large scale and in a high yield (95.8%) through the direct nitridation of Ga–Na_2SO_4 mixtures. This preparation method is also applicable to some other low-melting-point-metal oxides. The simplicity of the process and the range potential applications of the products would make this study very interesting.

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