A simple synthesis of Ga$_2$O$_3$ and GaN nanocrystals†

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The synthesis of gallium oxide and nitride nanocrystals is challenging. Herein, a forced hydrolysis route is developed to synthesize $\alpha$-GaOOH and the morphology control of nanocrystals is realized by adjusting the ratios of ionic strength in the synthesis system. The as-prepared $\alpha$-GaOOH nanorods can be transformed into $\alpha$-Ga$_2$O$_3$ nanorods upon calcination and can be further transformed into GaN nanocrystal assemblies through nitridation at elevated temperatures, which provides a top-down strategy to gallium oxide and nitride nanocrystals. The synthesis results are investigated by means of X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The optical properties, i.e. ultra-violet visible absorption (UV-vis) and photoluminescence, of as-obtained $\alpha$-Ga$_2$O$_3$ nanocrystals with different morphologies are examined and the morphology-property relationship is discussed.

According to these reports, it can be seen that the synthesis of GaN nanostructures always involves expensive and/or poisonous reagents, templates or substrates, and complicated processes. It is known that the nitridation of Ga$_2$O$_3$ represents a most simple strategy to free-standing GaN material. Theoretically, the morphology of parent Ga$_2$O$_3$ material can be preserved under controlled nitridation conditions, which provides a top-down morphology control strategy to GaN. It has been already reported that Ga$_2$O$_3$ nanorods can be synthesized via a thermal decomposition method using GaOOH nanorods. Moreover, GaN nanoparticles can be produced from Ga$_2$O$_3$ nanoparticles under a flow of ammonia gas at elevated temperatures.

Inspired by these achievements, we herein report a so-called forced hydrolysis route to GaOOH nanorods, which can be transformed to Ga$_2$O$_3$ nanorods through calcination and further transformed to GaN nanocrystal assemblies through nitridation. During the forced hydrolysis process, the hydroxyls are produced from urea decomposition and morphology control of GaOOH is realized by adjusting the ratio of ionic strength in the synthesis system.

Experimental

Synthesis of Ga$_2$O$_3$ and GaN samples

All the chemical reagents were of analytical reagent grade and directly used without further purification. GaOOH was prepared via a forced hydrolysis route starting from solution containing Ga(NO$_3$)$_3$ and NaNO$_3$ with different ionic strength ratios (see below for details).

Ionic strength ($I$) is calculated by the formula of $I = \frac{1}{2} \sum \frac{m_B Z_B^2}{mol}$, where $m_B$ is the molality of an ion $B$ in the solution and $Z_B$ is its charge number (positive for cations and...
negative for anions). The ratio of ionic strength (R) is defined as
\[ R = \frac{I_1}{I_2} \]
where \( I_1 \) represents the ionic strength of Ga(NO₃)₃ in the
solution and \( I_2 \) represents the ionic strength of NaNO₃ in the
solution.

In a typical synthesis, an appropriate amount of
Ga(NO₃)₃·nH₂O and urea were dissolved into a small amount of
deonized water (the molar ratio of Ga(NO₃)₃·nH₂O and urea
being kept at 1:6) and heated to 90 °C. More deionized water
was then added to reach a final molarity of urea is 0.18 mol L⁻¹
(Ga³⁺ of 0.03 mol L⁻¹) and the temperature was kept at 90 °C for
9 h to initiate forced hydrolysis. The solid product was centri-
fuged, thoroughly washed, dried and defined as GaOOH (R = ∞).
The as-obtained GaOOH was calcined in the vacuum at 450 °C to
derive Ga₂O₃, which was further nitridized in NH₃ flow
(100 mL min⁻¹) at 950 °C for 6 h to derive GaN. With the addition
of NaNO₃ into Ga(NO₃)₃·nH₂O solution at different ionic strength
ratios, GaOOH products (R = 3, 2, 1, 0.5, 0.3 or 0.2), were ob-
tained, which could also be transformed to Ga₂O₃ and GaN
samples (R = 3, 2, 1, 0.5, 0.3 or 0.2) via identical procedures.

For reference, commercial Ga₂O₃ (defined as Raw) was
nitridized at 950 °C for 6 h to derive GaN.

Characterization of Ga₂O₃ and GaN samples
The X-ray diffraction (XRD) patterns of samples were acquired
on a Rigaku Smart Lab 3 kW powder diffractometer with Cu Kα
radiation (λ = 0.1542 nm) at a scanning rate of 6° min⁻¹.

The specific surface areas of samples were determined through
N₂ physisorption at 77 K on a Quantachrome iQ-MP gas adsorption analyzer.

Scanning electron microscopy (SEM) images of Ga₂O₃ and GaN
samples were obtained on a JSM-7500F electron microscope.

Transmission electron microscopy (TEM) and high-
resolution transmission electron microscopy (HRTEM) images
of Ga₂O₃ and GaN samples were obtained on a FEI Tecnai G²
F20 electron microscope at 200 kV. Alcohol suspensions con-
taining the Ga₂O₃ or GaN were dropped onto a carbon-coated
copper grid, followed by evaporation at ambient temperature.

The Raman spectra of Ga₂O₃ and GaN were recorded on
a Renishaw InVia Raman spectrometer with the green line of an
Ar-ion laser (514.53 nm) in micro-Raman configuration.

Diffuse reflectance ultra-violet visible absorption (UV-vis)
spectra of Ga₂O₃ and GaN samples were performed on a Var-
ian Cary 300 UV/vis spectrophotometer.

Photoluminescence spectra of Ga₂O₃ and GaN samples were
acquired on a Spex FL201 fluorescence spectrophotometer. Self-
supporting wafers of samples (ca. 100 mg) were excited by
270 nm laser and the spectra were recorded in vacuum at
ambient temperature.

Results and discussion
The XRD patterns of GaOOH, Ga₂O₃ and GaN samples prepared at
R = 1 are shown in Fig. 1. It can be seen that pure orthorhombic
phase α-GaOOH is obtained from forced hydrolysis (JCPDS no. 06-
0180; a = 4.58 Å, b = 9.80 Å, c = 2.97 Å). GaOOH can be
transformed to pure hexagonal phase α-Ga₂O₃ (JCPDS no. 06-
0503; a = b = 4.98 Å, c = 13.43 Å) upon calcination at 450 °C and
Ga₂O₃ can be transformed to pure hexagonal phase GaN (JCPDS
no. 50-0792; a = b = 3.19 Å, c = 5.19 Å) upon nitridation at 950 °C.
These results clearly demonstrate the feasibility of Ga₂O₃ and GaN
synthesis through a so-called top-down strategy.

Fig. 2 shows the XRD patterns of Ga₂O₃ samples synthesized via
forced hydrolysis at different R values and followed by calcination. All the samples exhibit similar diffraction peaks of
α-Ga₂O₃ (JCPDS no. 06-0503), a monoclinic system and C2/m
space group with a = b = 4.98 Å and c = 13.43 Å as its cell
parameters.²⁷ No diffraction peaks corresponding to impurity
phases can be observed in all cases. We notice that, however,
the intensities of diffraction peaks of Ga₂O₃ samples synthe-
sized at different R values are different, indicating that different
morphologies and/or crystallinities were obtained for these
Ga₂O₃ samples. With increasing R value from 0.2 to 1, the

Fig. 1 XRD patterns of GaOOH, Ga₂O₃ and GaN prepared at R = 1.

Fig. 2 XRD patterns of Ga₂O₃ synthesized at different R values and
Raw Ga₂O₃.
relative crystallinity increases distinctly, while the relative crystallinity decreases with further increase in $R$ value. That is, Ga$_2$O$_3$ with highest crystallinity can be obtained with optimized ionic strength ratio of 1 during forced hydrolysis.

Raman spectroscopy is further employed to determine the structure of as-prepared Ga$_2$O$_3$ samples. As shown in Fig. S1,† Raman bands at 410, 560 and 700 cm$^{-1}$ are observed in the 300–1000 cm$^{-1}$ region, corresponding to the $E_g$, $A_{3g}$ and $E_g$ modes of $z$-Ga$_2$O$_3$, respectively. The Raman bands broadening and the noticeable shifts of bands at 700–710 cm$^{-1}$ are due to the presence of surface defects on the samples.

The XRD patterns of GaN samples from the nitridation of different Ga$_2$O$_3$ samples are shown in Fig. 3. Pure GaN phase of wurtzite structure and $P6_3mc$ space group with $a = b = 3.189$ Å and $c = 5.185$ Å as its cell parameters is obtained in all cases. We also notice the different intensities of diffraction peaks, similar to the trend observed for Ga$_2$O$_3$ samples. It can be proposed that the morphologies and crystallinities of Ga$_2$O$_3$ samples are preserved, at least partially preserved, through nitridation at elevated temperature of 950 °C. Raman spectra of GaN samples are presented in Fig. S2† and a series of Raman bands can be observed in the 300–1000 cm$^{-1}$ region. The band at 420 cm$^{-1}$ is related to the N-rich structure of GaN, while the shifts of other Raman bands, e.g. at 515, 595 and 695 cm$^{-1}$, compared with standard hexagonal GaN, should be related to the formation of abundant defects on the surface.

The SEM images of Ga$_2$O$_3$ samples synthesized by forced hydrolysis at different $R$ values are shown in Fig. 4. It is very clear that different morphologies are obtained at different ratios of ionic strength during forced hydrolysis, i.e. $R$ values. At $R = \infty$, Ga$_2$O$_3$ crystals appear as spindle-like nanorods with two narrow sides and a wide center (Fig. 4a). At $R = 3$ and 2, Ga$_2$O$_3$ crystals appear as nanorods with the same broad sides and center (Fig. 4b and c). With decreasing $R$ value to 1, Ga$_2$O$_3$ crystals transform to dumbbell-shaped nanorods with two wide sides and narrow center (Fig. 4d). Further decrease in the ratio of ionic strength during forced hydrolysis ($R = 0.5$ and 0.3) results in the exfoliation of nanorods to nanoplates and strips and fragments (Fig. 4e and f). At $R = 0.2$, the Ga$_2$O$_3$ crystals are totally broken up to fragments. According to the SEM images of Ga$_2$O$_3$ samples synthesized at different $R$ values, we can infer that the crystallinities of Ga$_2$O$_3$ samples vary with $R$ values. The highest crystallinity of Ga$_2$O$_3$ sample is obtained at the $R$ value of 1, in accordance with the results from XRD patterns (Fig. 2). The surface areas of Ga$_2$O$_3$ samples synthesized at different $R$ values are measured to be in the range of 30–50 m$^2$ g$^{-1}$, distinctly higher than commercial Ga$_2$O$_3$ (15 m$^2$ g$^{-1}$).

Fig. 5 shows the SEM images of GaN samples obtained from the nitridation of Ga$_2$O$_3$ samples. It is seen that the overall shape of GaN sample follows its Ga$_2$O$_3$ precursor. However, after careful observation, we find that some tiny nanoparticles do exist on the external surface of GaN crystals. These observations indicate that nitridation starts from a local point of Ga$_2$O$_3$ crystal. The surface areas of as-obtained GaN samples are measured to be 40–60 m$^2$ g$^{-1}$, even higher than parent Ga$_2$O$_3$ (30–50 m$^2$ g$^{-1}$) due to the formation of tiny nanoparticles on the surface. To confirm the phase purity of as-obtained GaN samples, the energy-dispersive X-ray mapping analysis was
performed on representative GaN sample \((R = 1)\). As shown in Fig. S3,† the homogeneous distribution of Ga and N species in selected GaN crystal grain is clearly observed \((\text{Ga/N} = 0.86; \text{Ga/N} < 1 \text{ due to the presence of N-containing impurities})\), ruling out the formation of metallic Ga islands from nitridation at high temperature of 950 °C.

For a more clear view of the morphology changes during nitridation, TEM images of Ga\(_2\)O\(_3\) and GaN samples synthesized at \(R = 1\) are shown in Fig. 6. A typical Ga\(_2\)O\(_3\) crystal assembly appears as a nanorod with length of 2 μm and diameter of 0.4 μm (Fig. 6a). In the HRTEM images (Fig. 6b and c), clear lattice fringes with interplanar spacing of 0.249 nm are observed, corresponding to the \((110)\) planes of Ga\(_2\)O\(_3\) crystal. After nitridation, the overall shape of Ga\(_2\)O\(_3\) is well preserved (Fig. 6d), in accordance with SEM observations. It is also found that the GaN crystal assembly is composed of tiny nanoparticles with sizes of a few to a dozen nanometers. Accordingly, some nanoscale mesopores can be observed in GaN crystal assembly. HRTEM images (Fig. 6e and f) reveal the lattice fringes with interplanar spacing of 0.276 nm, corresponding to the \((100)\) planes of GaN crystal.

On the basis of SEM (Fig. 4) and TEM observations (Fig. 6), we demonstrate that Ga\(_2\)O\(_3\) samples with different morphologies can be prepared via controlling the ratio of ionic strength during forced hydrolysis. With decreasing \(R\) value, the morphology of Ga\(_2\)O\(_3\) crystals gradually transforms from spindle-like to dumbbell-shaped nanorods and then to exfoliated fragments, which gives us a hint on the formation process of Ga\(_2\)O\(_3\) sample. A schematic diagram of morphology-controlled synthesis of Ga\(_2\)O\(_3\) via forced hydrolysis route is summarized in Fig. 7. In the first step, different ratios of Ga(NO\(_3\))\(_3\)·nH\(_2\)O, NaNO\(_3\) and urea are mixed in deionized water and heated at 90 °C to form unstable Ga(OH)\(_3\) transition state. Then, the unstable Ga(OH)\(_3\) transition state crystallizes to different morphologies of α-GaOOH at 90 °C with the presence of different concentrations of sodium ions as structure-directing and mineralizing agents. In the final step, GaOOH is transformed to α-Ga\(_2\)O\(_3\) through calcination in vacuum, with its morphology well preserved. Besides, the as-obtained α-Ga\(_2\)O\(_3\) can be transformed to GaN with overall morphology well preserved (Fig. 6).

The optical properties of as-obtained α-Ga\(_2\)O\(_3\) samples with different morphologies are examined to explore the possible morphology-dependent effects. The UV-vis spectra of α-Ga\(_2\)O\(_3\) synthesized at different \(R\) values are shown in Fig. 8. Commercial α-Ga\(_2\)O\(_3\) sample (Raw) shows significant absorption in the ultraviolet region with edge up to ~290 nm, corresponding to the

Fig. 5 SEM images of GaN from the nitridation of Ga\(_2\)O\(_3\) synthesized at different \(R\) values: \(R = \infty\) (a); \(R = 3\) (b); \(R = 2\) (c); \(R = 1\) (d); \(R = 0.5\) (e); \(R = 0.3\) (f); \(R = 0.2\) (g) and Raw Ga\(_2\)O\(_3\) (h).

Fig. 6 TEM images (a, d), HRTEM images (b, e) and enlarged view of HRTEM images (c, f) of Ga\(_2\)O\(_3\) and GaN samples synthesized at \(R = 1\).

Fig. 7 Schematic diagram of morphology-controlled synthesis of Ga\(_2\)O\(_3\) via forced hydrolysis route.
band gap of ~4.3 eV. While for \( \alpha \)-Ga\(_2\)O\(_3\) samples prepared via forced hydrolysis, two absorption peaks can be distinguished, i.e. intrinsic absorption with edge up to ~260 nm (4.8 eV) and sub-band absorption with edge up to ~360 nm (3.5 eV). The sub-band absorption should be related with the existence of abundant defect sites in \( \alpha \)-Ga\(_2\)O\(_3\), e.g. oxygen vacancies as proposed in other oxide semiconductors.\(^{30,31}\) It is seen that the highest absorption with edge up to ~360 nm is obtained with \( \alpha \)-Ga\(_2\)O\(_3\) sample at \( R = 1 \), indicating its highest defect site concentration.

For GaN samples from the nitridation of \( \alpha \)-Ga\(_2\)O\(_3\) samples, significant absorption in the ultraviolet and visible region is observed (Fig. S4†). The band-edge energy cannot be distinguished due to the overlap by sub-band absorption as well as the serious light scattering effects caused by the formation of mesoporous structure (Fig. 5 and 6).

The photoluminescence properties of \( \alpha \)-Ga\(_2\)O\(_3\) samples synthesized at different \( R \) values are examined. It is known that the photoluminescence emissions are originated from the radiative recombination of photo-generated electrons and holes on semiconductors. Two major photo-physical processes, i.e. direct band-band transition and indirect transition from trapping states, can give rise to photoluminescence signals. Under 270 nm ultraviolet light excitation, a broad photoluminescence signal from 350 to 700 nm (centered at 500 nm) is observed for commercial \( \alpha \)-Ga\(_2\)O\(_3\) sample (Fig. 9). While for \( \alpha \)-Ga\(_2\)O\(_3\) samples prepared via forced hydrolysis followed by calcination, two significant photoluminescence signals at 460 (blue photoluminescence) and 600 nm (orange photoluminescence) are observed. The blue photoluminescence signal should be originated from the recombination of photogenerated electrons on donors and holes on acceptors while the orange photoluminescence from the recombination on deep trapping states.\(^{32,33}\) Undoubtedly, all these two photoluminescence signals are associated with the defect sites in as-prepared \( \alpha \)-Ga\(_2\)O\(_3\) samples, which distinguish them from commercial sample. In this context, the intensity of photoluminescence signals is determined by both the defect sites and the crystallinity of the sample.

We find that the sequence of photoluminescence intensity (Fig. 9) correlates well with the optical absorption (Fig. 8), both of which indicate the morphology-dependent optical properties of \( \alpha \)-Ga\(_2\)O\(_3\) samples. At \( R = 1 \), the highest photoluminescence intensity is obtained, several times higher than commercial \( \alpha \)-Ga\(_2\)O\(_3\) sample.

We also investigate the optical properties of GaN samples prepared from the nitridation of \( \alpha \)-Ga\(_2\)O\(_3\) samples and the results are shown in Fig. S5†. Significant photoluminescence signals at 380 and 450 nm are observed for all samples in the 350–480 nm region, and the highest photoluminescence intensity is obtained with GaN (\( R = 1 \)). Besides, we cannot draw other convincing conclusions on the morphology-dependent effects due to the serious light scattering effects caused by the formation of mesoporous structure. Further researches on these issues are still in progress.

Conclusions

In summary, we have successfully developed a forced hydrolysis route to \( \alpha \)-GaOOH starting from inorganic gallium salt and urea as raw materials, and we have realized the morphology control by adjusting the ratios of ionic strength in the synthesis system, i.e. Ga\(^{3+}\)/Na\(^+\). The as-prepared \( \alpha \)-GaOOH nanorods can be transformed to \( \alpha \)-Ga\(_2\)O\(_3\) nanorods upon simple calcination with the morphology well preserved, and be further transformed to GaN nanocrystal assemblies through nitridation. This process provides a top-down strategy to Ga\(_2\)O\(_3\) and GaN nanocrystals. Typically, the morphology of as-obtained \( \alpha \)-Ga\(_2\)O\(_3\) crystals gradually transform from spindle-like to dumbbell-shaped nanorods and then to exfoliated fragments with decreasing ratios of ionic strength in the synthesis system. While for the GaN samples prepared from nitridation at elevated temperature, the overall shape of \( \alpha \)-Ga\(_2\)O\(_3\) precursor can be preserved and nanoscale mesopores originated from nanoparticles assembling are clearly observed.

The UV-vis absorption and photoluminescence properties of Ga\(_2\)O\(_3\) crystals with different morphologies are examined, and the
results clearly demonstrate the morphology-dependent effects. The methodology presented here may be extended to the synthesis and applications of other oxide and nitride semiconductors.

Conflicts of interest

There are no conflicts to declare.

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Notes and references