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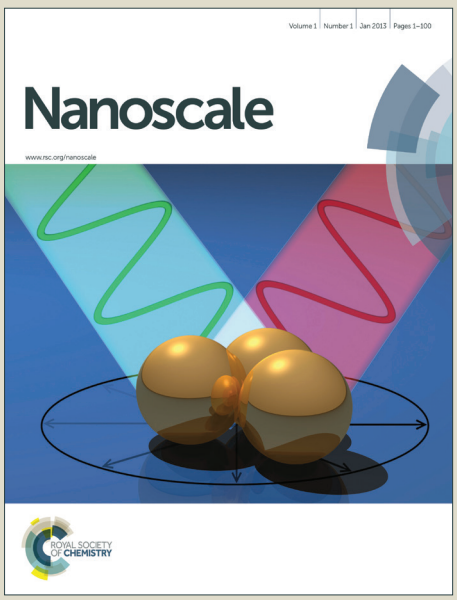

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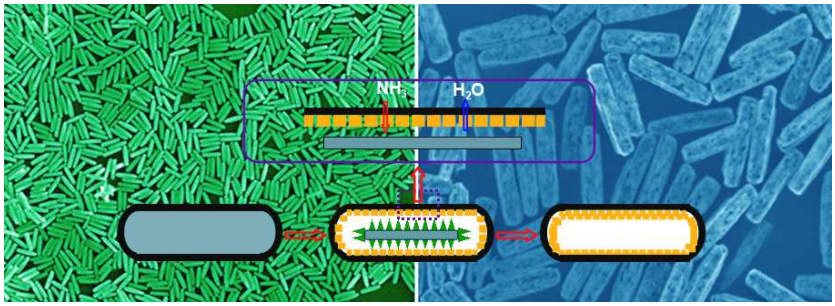
Graphical Abstract



Carbon-coated GaN hollow nanospindles with uniform morphology and good structural stability are facilely prepared by nitridizing solid carbon-coated GaOOH nanospindles in an ammonia atmosphere at 800 °C for 2 h.

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ARTICLE TYPE

Carbon nanocoating: an effective nanoreactor towards well-defined carbon-coated GaN hollow nanospindles†

Wenlong Yang,[a‡] Yanrong Wang,[a‡] Atangana Etogo,[a] Jiqiang Ning,[b] Yunlong Xie[a] and Yong Hu*[a]

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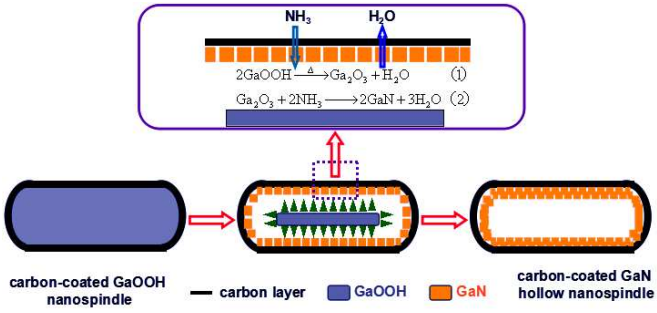
Carbon-coated GaN hollow nanospindles with uniform morphology and good structural stability are facilely prepared by nitridizing solid carbon-coated GaOOH nanospindles in an ammonia atmosphere at 800°C for 2 h. The carbon nanocoating acts nanoreactor which not only preserves the spindle-like morphology, but also prevents GaN particles from growing during the thermal treatment. The significant advantage is that the hollow nanostructures so obtained exhibit superior resistance to distortion, collapse, and shrinkage.

As one of the most important III-V semiconductors with a wide direct band gap of 3.4 eV, gallium nitride (GaN) has attracted great research interests because of its potential applications in optoelectronic devices, such as prospective blue lasers, optical communication, full-colored, flat panel displays, and so on.[1] Up to now, GaN nanostructures with various morphologies and structures, including nanoparticles, nanorods, nanowires, nanobelts, nanotubes, and hollow nanospheres, have been successfully prepared.[2] Especially, hollow structures have attracted growing research interests due to their outstanding characteristics, such as low density, high surface-to-volume ratio, and low coefficients of thermal expansion for their potential applications in adsorbents, catalysis, drug delivery, microreactors, etc.[3] Templating strategy is considered to be a conveniently and broadly employed method for the fabrication of hollow structures.[4] For example, GaN hollow spheres have been prepared from surface-layer-absorption (SLA) templating technique by using monodispersed carbon spheres as templates.[5] However, the distortion, collapse, and shrinkage of the GaN hollow structures, taking place unavoidably during the core removal process by high temperature heating or chemical etching, are not favorable for their wide applications in experiment and in practice. Therefore, it is highly desirable to develop new methods to synthesize well-defined GaN hollow structures.

It is well known that amorphous carbon widely serves as an interesting coating material for the purpose of improving corrosion resistance, thermal stability, adsorbability, or electronic properties of the coated materials.[6] And, it can be easily obtained via inexpensive and environmentally benign hydrothermal processes using glucose as precursor. Herein, we present a novel strategy for the preparation of uniform carbon-coated GaN (C-GaN) hollow nanospindles by nitridizing solid carbon-coated GaOOH (C-GaOOH) nanospindles in NH_3 flow at 800 °C for 2 h.

This straightforward synthesis strategy is schematically depicted in Scheme 1, and the detailed experimental procedure is described in ESI†. Firstly, solid C-GaOOH nanospindles were obtained via a facile one-pot hydrothermal reaction. Secondly, uniform C-GaN hollow nanospindles were synthesized by nitridizing C-GaOOH nanospindles in NH_3 flow at 800 °C for 2 h. The whole reaction process can be divided into two steps: (i) C-GaOOH nanospindles were gradually converted into C-Ga_2O_3 core-shell nanospindles at a relatively low temperature of around 450°C via the thermal dehydration reaction: $2GaOOH \rightarrow Ga_2O_3 + H_2O$.[7] (ii) Ga_2O_3 reacted with NH_3 at a desired temperature: $G_2O_3 + 2NH_3 \rightarrow 2GaN + 3H_2O$.[8] During nitridization, the carbon nanocoating acts as a nanoreactor as well as a protective layer for the fabrication of C-GaN hollow structures, effectively preventing samples from distortion, collapse, and shrinkage during the heating process at elevated temperature. The carbon nanocoating is crucial for the formation of well-defined C-GaN hollow structures, whose role is similar to the mesoporous silica shell in the synthesis of hollow iron oxide core.[9] The hollow structure was generated by a thermal treatment in NH_3 flow, leaving an thin GaN layer firmly adhered to the carbon shell.[10] As a result, GaN hollow nanospdiles were obtained with both uniform size distribution and good structural stability.



Scheme 1 Schematic illustration of the formation of C-GaN hollow nanospindles by nitridizing solid C-GaOOH nanospindles in NH_3 atmosphere at 800 °C for 2 h.

The phase composition and structure of the as-prepared C-GaOOH nanospindles and C-GaN hollow nanospindles were examined by X-ray powder diffraction (XRD), as shown in Fig.1. For C-GaOOH nanospindles, all the strong reflection peaks can

be well indexed to the orthorhombic phase of GaOOH (JCPDS card no. 06-0180, a = 4.58 Å, b = 9.80 Å, c = 2.97 Å). No impurity peaks are detected, implying that the final products are of pure phase. Therefore, the use of glucose in the hydrothermal process has no effect on the crystalline phase of GaOOH. For C-GaN hollow nanospindles, the pattern obviously consists of the diffraction peaks of the wurtzite structure of GaN (JCPDS card no. 76-0703, a = 3.190 Å, c = 5.189 Å). No diffraction peaks from other crystalline forms of GaN can be detected, which indicates a complete conversion of C-GaOOH templates and high purity of the products. Additionally, the XRD patterns of the as-prepared pure GaN obtained from GaOOH nanospindles via the same annealing process in NH_3 flow are shown in Fig. S1(see ESI†).

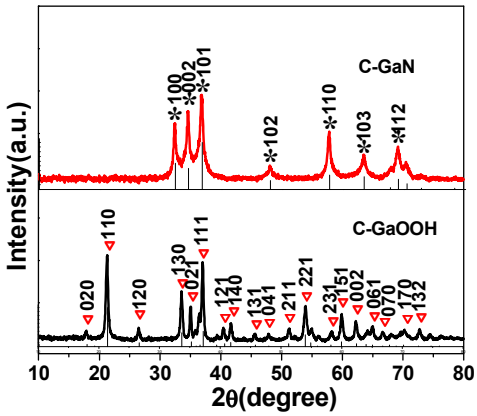


Fig. 1 XRD patterns of the as-prepaed C-GaOOH nanospindles and C-GaN hollow nanospindles.

The morphology and structure of the C-GaOOH nanospindles and C-GaN hollow nanospindles were studied by the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images. Fig. 2A displays the SEM image of the C-GaOOH nanospindles obtained via a facile one-pot hydrothermal reaction. It can be seen that the as-prepared C-GaOOH nanospindles exhibit uniform morphology and size distribution typically 120 nm in diameter and 550 nm in length. Fig. 2B shows an SEM image of the as-prepared C-GaN hollow nanospindles derived from nitridizing C-GaOOH nanospindles without any impurity particles or aggregates. The morphology and structure of C-GaOOH nanospindles and C-GaN hollow nanospindles are further elucidated by TEM images, as shown in Fig. 2C and D. From the high-resolution TEM (HRTEM) image of a section of a single C-GaOOH nanospindle (inset in Fig. 2C), it can be clearly seen that the GaOOH nanospindle is coated with a layer of amorphous carbon about 5 nm in thickness. Fig. 2D reveals well-defined C-GaN hollow nanospindles. The void interior indicates that the GaOOH nanospindles are fully converted into C-GaN hollow nanospindles after annealing in NH_3 flow at 800 °C for 2 h. For comparison, SEM and TEM images of pure GaOOH and GaN obtained with similar methods without the addition of glucose are provided in Fig. S2 (ESI†). It can be seen that only some porous and distorted GaN nanospindles are obtained in the absence of carbon nanocoating, and no well-defined hollow nanostructures are observed. This result further demonstrates the vital role of the carbon layer for the preparation of well-defined GaN hollow structures.

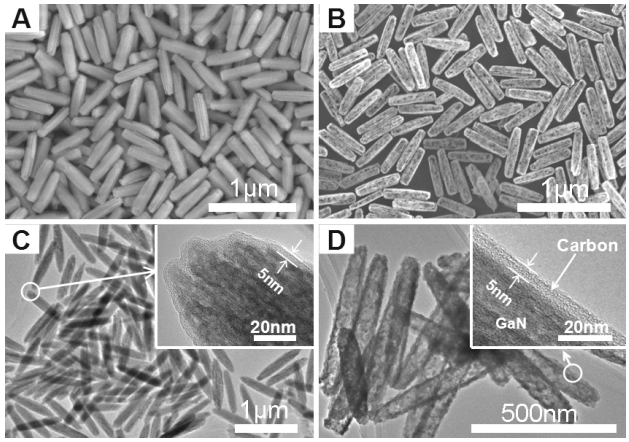


Fig. 2 SEM images of the as-prepared solid C-GaOOH nanospindles (A) and C-GaN hollow nanospindles (B), and TEM and HRTEM (inset) images of the C-GaOOH nanospindles (C) and C-GaN hollow nanospindles (D).

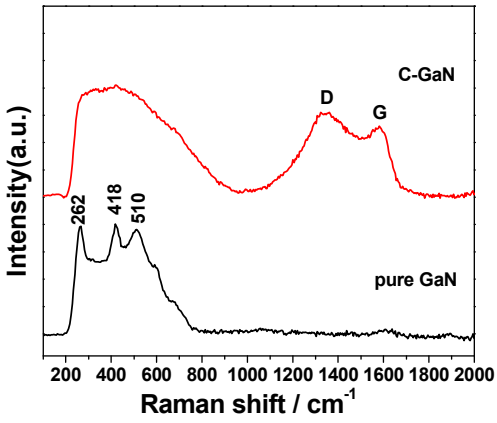


Fig. 3 Raman spectra of the as-prepaed pure GaN nanospindles and C-GaN hollow nanospindles.

Fig. 3 display the Raman spectra of the as-prepared pure GaN nanospindles and C-GaN hollow nanospindles. The Raman spectrum of the pure GaN nanospindles shows Raman scattering modes centered at 265, 418 and 510 cm^{-1}. The modes at about 265 and 418 cm^{-1} are generally assigned to the zone-boundary phonon activated by crystal disorders, finite size effects and the acoustic overtone of wurtzite GaN.[11] The Raman mode at 510 cm^{-1} also agrees with the phonon vibration frequencies observed in GaN nanostructures.[8] Instead of these vibration modes, a broad vibration band is observed in the spctrum from C-GaN hollow nanospindles, indicating a further disturbance of the GaN lattice in the hollow nanostructure. In addition to the characteristic bands for GaN, the Raman spectrum of the C-GaN hollow nanospindles shows the fundamental D and G bands of carbon at around 1344 and 1578 cm^{-1}. The G-band at around 1578 cm^{-1} is attributed to the characteristic ordered graphitic-like carbon, and

the D-band at around 1344 cm^{-1} indicates the presence of defects within thehexagonal graphitic structure.[12] The intensity ratio of D- and G- band (I_D/I_G) is indicative of the degree of graphitization, and we obtain a ratio of 1.22 from the Raman spctrum. The broad D-band and high intensity ratio of I_D/I_G suggest a low degree of graphitization.[13] Additionally, photoluminescence (PL) spectrum measurement for the as-prepared C-GaN hollow nanospindles was collected at room temperature to evaluate their optical quality. A representative PL spectrum of the product (Fig. S3, see ESI†) displays a band edge emission peak at around 358 nm and a yellow luminescence band centered at around 547 nm. The emission band at around 358 nm is ascribed to the band edge emission peak of C-GaN hollow nanospindles.[14] However, the origin of the deep acceptors responsible for yellow luminescence is still not identified, which is maybe attributed to the several reasons, such as, the presence of various defects within the GaN crystals,[15] carbon impurity or a complex involving carbon,[16] or the edge dislocation density.[17]

In summary, we have demonstrated a novel strategy for the preparation of well-defined C-GaN hollow nanospindles with uniform size distribution and good structural integrity. Carbon coated GaOOH nanospindles were used as the precursor for the synthesis of C-GaN hollow nanospindles. The precursor was firstly obtained via a facile one-pot hydrothermal reaction, and then nitridized in NH_3 flow at a temperature of 800 °C for 2 h to produce the hollow nanostructures. Compared with traditional template methods, the carbon nanocoating is critical for the fabrication of the well-defined C-GaN hollow nanospindles due to its superior resistance to distortion, collapse, and shrinkage. It is belived that this method can be extended to the synthesis of other hollow nanostructures with various morphologies.

Acknowledgements

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Notes and references

[a] *Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Institute of Physical Chemistry, Zhejiang Normal University, Jinhua, 321004, P.R.China. E-mail: yonghu@zjnu.edu.cn*

[b] *Department of Physics and HKU-CAS Joint Laboratory on New Materials, The University of Hong Kong, Pokfulam Road, Hong Kong, P.R. China.*

‡*These authors contributed equally to this work.*

† Electronic Supplementary Information (ESI) available: Detailed experimental procedures, additional SEM images and XRD pattern, See DOI: 10.1039/b000000x/

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