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Shape-Controlled Synthesis of GaN Nanorods and Their Photoluminescence Property

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In this paper, an atom-economical and eco-friendly chemical synthetic route was developed to synthesize wurtzite GaN nanorods by the reaction of $NaNH_2$ and the as-synthesized orthorhombic GaOOH nanorods in a stainless steel autoclave at 650 °C. The lengths of the GaN nanorods are in the range of 400-600 nm and the diameters are about 100-300 nm. It is interesting that the initial GaOOH structural motifs were unaffected by the high temperature chemical transformations process. The photoluminescence (PL) of GaN nanorods exhibits emission peak in the blue region, which is possibly attributable to the existence of defect.

Keywords: GaN nanorods, GaOOH nanorods, Photoluminescence.

INTRODUCTION

Extensive research on refractory group III nitride semiconductors continues at a dizzying pace, motivated to a large extent by the development of new blue- and green-light-emitting diodes and lasers in practical optoelectronic devices[1]. The recent development of commercial blue-light emitters based on GaN has propelled these materials into the mainstream of interest. GaN is well-known for its excellent optoelectronic properties with direct and wide bandgap, high mobility and excellent thermal stability[2,3]. Furthermore, GaN materials have recently gained much more attentions because of the capability to promote hydrogen production by water splitting [4].

GaN materials have been prepared by many methods, such as vapor deposition[5], metal-organic chemical vapor deposition[6], molecular beam epitaxy[7], halide vapor-phase epitaxy[8], magnetron sputtering[9], chemical thermal-evaporation process[10], etching method[11] and ammonolysis route[12]. Up to now, many structures of GaN including nanoparticles[13], nanowires[14], microrods[15], nanobelts[16], hollow spheres[17] and tubes[18] have been successfully synthesized.

It is well known that the size- and shape-controlled synthetic methodologies are of great interest in material properties[19]. Thus, compounds with the same compositions, but different morphologies, are exhibiting remarkable differences in their properties. The properties of GaN semiconductors are strongly dependent on the shape, size and dimensionality of the particles. It would be interesting to synthesize GaN with various morphologies for different applications. In this paper, we reported an economical and eco-friendly chemical synthetic method for synthesis of wurtzite GaN microrods. The preparation of wurtzite GaN nanorods involved two steps: first, hydrothermal synthesis of orthorhombic GaOOH nanorods at 190 °C for 12 h; second, preparation of GaN nanorods using $NaNH_2$ and the as-prepared orthorhombic GaOOH nanorods as reactants in a stainless steel autoclave at 650 °C for 5 h.

EXPERIMENTAL

All the reagents used in the experiment were analytically pure, purchased from Shanghai Chemical Reagent Company and used without further purification.

Synthesis of GaOOH nanorods: In a typical synthesis, under continually stirring, 1.026 g of $GaCl_3$ (5 mmol) was dissolved in a mixture of 10 mL of deionized water and 20 mL of diethyl ether. After 5 min, 3.25 g of sodium azide was introduced to the above solution. Then the solution was transferred into a 40 mL Teflon-lined autoclave. The autoclave was sealed, maintained at 190 °C for 12 h and then allowed to cool to room temperature naturally. The product was retrieved by filtration, washed several times with distilled water and absolute ethanol and dried under vacuum at 60 °C for 6 h.

Preparation of GaN nanorods: 1.03 g (10 mmol) of the as-prepared GaOOH nanorods and 0.63 g (16 mmol) of $NaNH_2$ were mixed and then put into a stainless steel autoclave. The autoclave was maintained at 650 °C for 5 h and then cooled to room temperature naturally. A yellow powder was retrieved by centrifugation, washed several times with dilute hydrochloric acid, distilled water and absolute alcohol and finally dried in a vacuum oven at 60 °C for 6 h.

Characterization: Powder X-ray diffraction (XRD) measurements were carried out with a Philips X'Pert diffractmeter (CuK_α λ = 1.541874 Å; Nickel filter; 40 kV, 40 mA). Field emission scanning electron microscope (FESEM) images were taken on a JEOL JSM-6300F SEM. Transmission electron microscopy (TEM) images, high-resolution transmission electron microscopy (HRTEM) images and selected area electron diffraction (SAED) patterns were performed on JEOL JEM-2010 microscope operating at 200 kV. Photoluminescence (PL) measurements were carried out on a Perkin-Elmer LS-55 luminescence spectrometer using a pulsed Xe lamp.

RESULTS AND DISCUSSION

Characterization of GaOOH nanorods: The morphologies and the structures of the product were checked by using field emission scanning electron microscope (FESEM), transmission electron microscopy (TEM). Typical FESEM and TEM images of the as-prepared GaN microrods are shown in Fig. 1. Fig. 1(a-b) show FESEM images of the as-prepared orthorhombic GaOOH, which clearly exhibits that the product consists of uniform nanorods with lengths in the range of 400-600 nm and diameters of about 100-300 nm. Fig. 1(c-d) is the representative TEM images of the GaOOH product, indicating that the nanorods are solid structure, about 500 nm in length. Fig. 1e displays the X-ray diffraction (XRD) pattern of the GaOOH microrods. It can be observed that orthorhombic phase of GaOOH formed in our synthesis. All the reflection peaks can be indexed as orthorhombic phase of GaOOH (JCPDS PDF No. 06-0180, a = 4.58 Å, b = 9.80 Å, c = 2.97 Å). No peaks of impurities were detected.

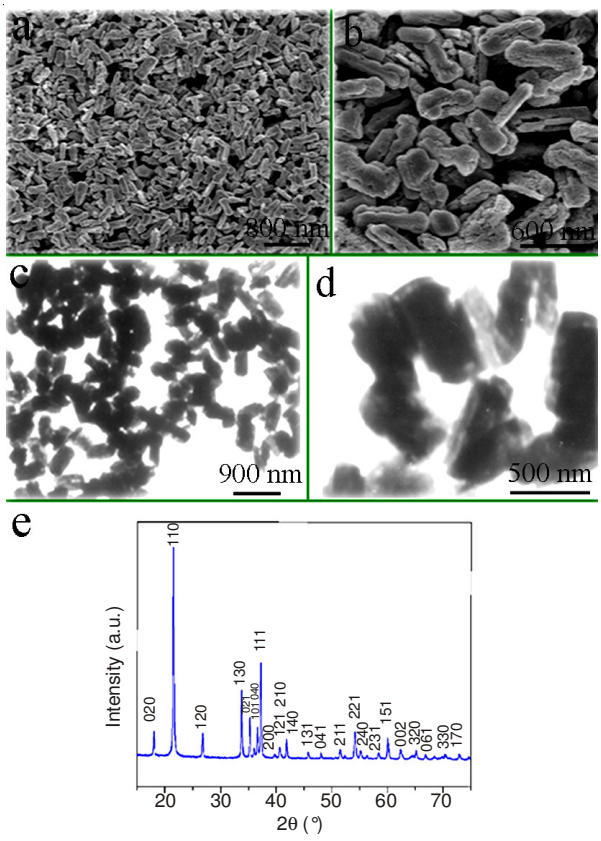

Fig. 1. (a-b) FESEM images, (c-d) TEM images, (e) XRD of GaOOH nanorods

Characterization of GaN nanorods: The GaN nanorods were prepared *via* a solid-state reaction using $NaNH_2$ and the as-prepared orthorhombic GaOOH nanorods as reactants in a stainless steel autoclave. Fig. 2 indicates the XRD pattern of the as-prepared GaN product. All the reflection peaks can be indexed as wurtzite GaN, which is in good agreement with the standard data (JCPDS PDF No. 74-0243, a = 3.195 Å, c = 5.182 Å). No peaks of impurities such as Ga2O3 and Ga were detected, revealing that the orthorhombic GaOOH precursor was completely converted into wurtzite GaN under the experimental conditions.

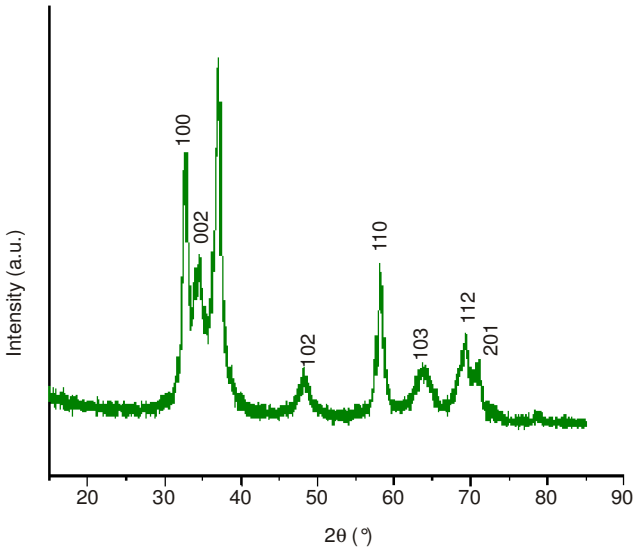

Fig. 2. XRD pattern of the as-prepared GaN nanorods

FESEM and TEM analyses were used to explore the morphology and crystal structure of the as-synthesized wurtzite GaN nanorods. Fig. 3(a-b) presents FESEM image of the GaN product. On the basis of these data, it can be observed that the sample consists of nanorods with lengths in the range of 400-600 nm and diameters of about 100-300 nm. Careful observation from the high magnification images (Fig. 3(c-d)) indicate that the rough surfaces of GaN nanoorods are made of densely packed GaN nanoparticles about 50-150 nm in sizes. Fig. 3(e-g) are the representative TEM images of the GaN nanorods, displaying that the product is solid structure, about 400-600 nm in length and 100-300 nm in diameter.

The structures of nanorods were investigated by high-resolution transmission electron microscopy (HRTEM) images and selected area electron diffraction (SAED). Fig. 4a is the TEM image of GaN nanorods. Fig. 4b is the corresponding SAED pattern obtained from the region labeled ellipse in Fig. 4a. The SAED pattern can be indexed to the typical (100), (110) and (010) planes of wurtzite GaN. Fig. 4c and d are the corresponding HRTEM images reveals the crystal planes have lattice spacing of about 0.275 nm corresponding to (100) plane of wurtzite GaN.

Luminescence property: GaN is one of the most promising optoelectronic semiconductors in solid-sate devices and its optical properties are directly related to its potential applications. The room temperature photoluminescence (PL) spectrum

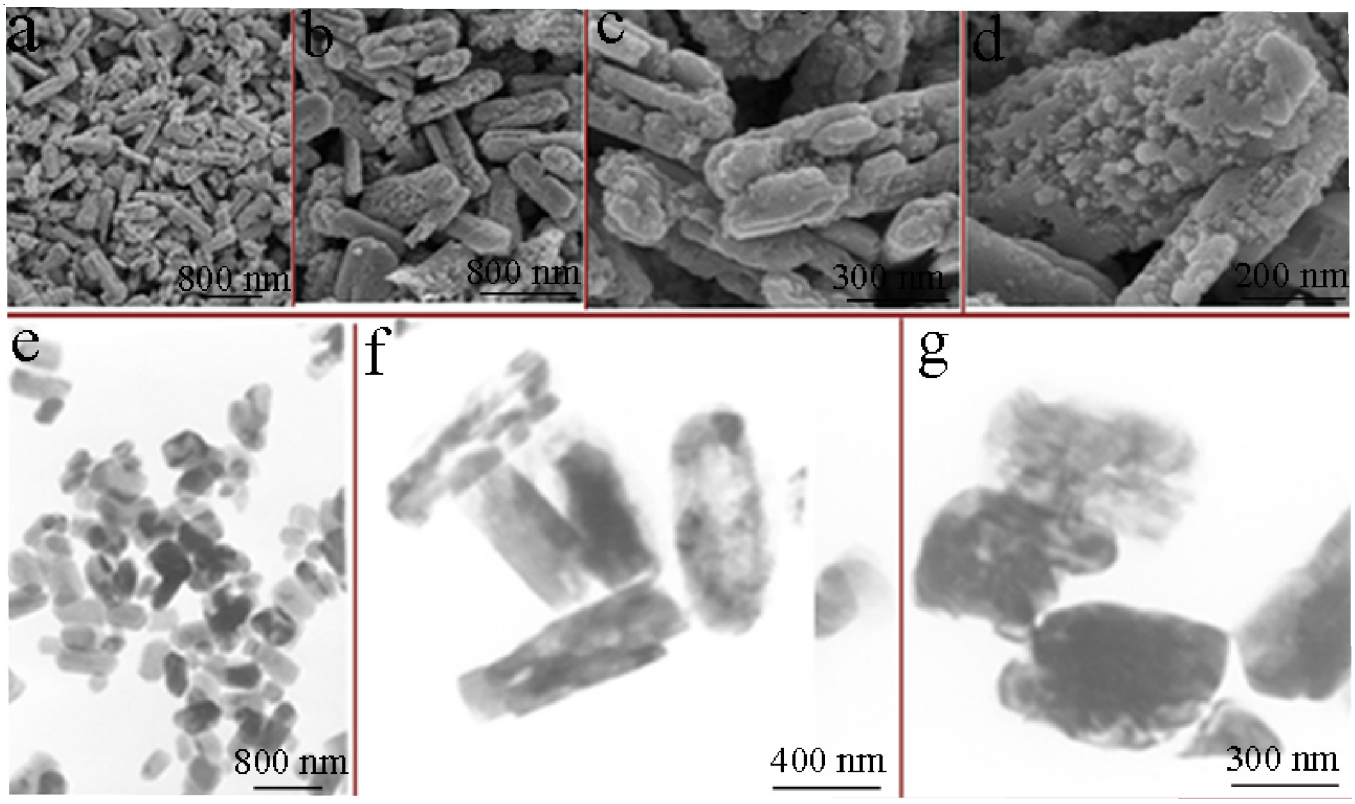

Fig. 3. (a-d) FESEM images, (e-g) TEM images of GaN nanorods

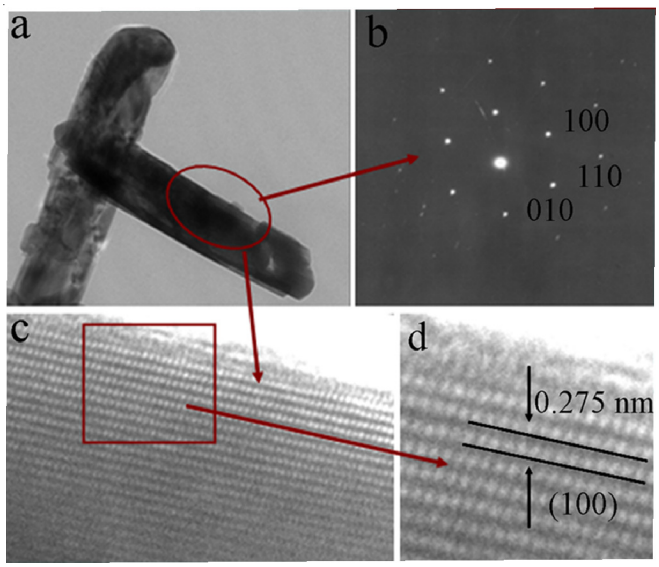

Fig. 4. (a) TEM image; (b) corresponding SAED pattern; (c-d) HRTEM images of the as-prepared GaN nanorods

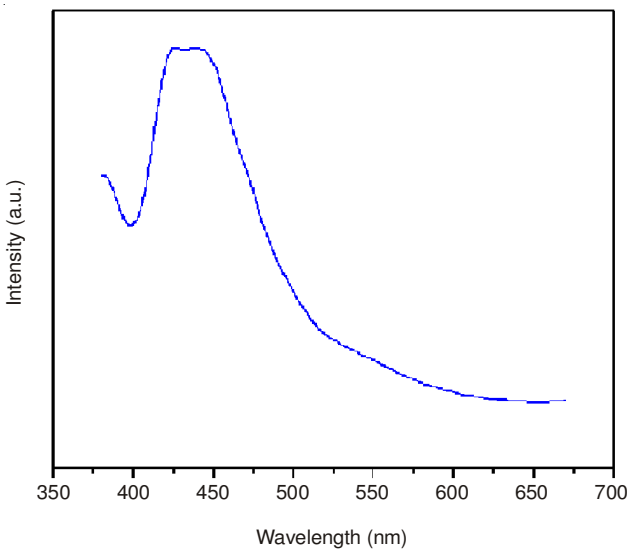

Fig. 5 Room-temperature photoluminescence (PL) spectrum of the as-prepared GaN nanorods

of the GaN nanorods recorded with excitation wavelength of 370 nm is shown in Fig. 5. The PL emission spectrum of the wurtzite GaN nanorods reveals an emission peak centered at 438 nm. The position of the PL emissions spectrum of GaN nanorods is possibly attributable to the existence of defect[20]. The defects, which can directly serve as radiative centers, may be helpful for electro-optical properties and extend the potential optical and optoelectronic application to the field of high-temperature electron devices.

Conclusion

We have demonstrated a convenient chemical route to synthesize wurtzite GaN nanorods. The synthesis of wurtzite GaN taper rods involved two steps: first, hydrothermal synthesis of GaOOH prismatic rods at 190 °C for 12 h; second, preparation of GaN taper rods using $NaNH_2$ and the as-prepared GaOOH prismatic rods as reactants at 650 °C for 5 h. GaOOH nanorods transformed into wurtzite GaN nonorods without destroying the 1D framework. The lengths

of the as-obtained wurtzite GaN are in the range of 400-600 nm and the diameters are about 200 nm. The photoluminescence measurements reveal that the as-prepared wurtzite GaN nanorods showed strong blue emission.

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