Supporting Information

for

Synthesis and Optical Properties of Gallium Phosphide Nanotubes

Qiang Wu, Zheng Hu,* Chun Liu, Xizhang Wang, and Yi Chen

Key Laboratory of Mesoscopic Chemistry of MOE, and Jiangsu Provincial Laboratory for NanoTechnology, Department of Chemistry, Nanjing University, Nanjing 210093, China

Yinong Lu

Laboratory of Electron Microscopy, College of Materials Science & Engineering, Nanjing University of Technology, Nanjing 210009, China

* The corresponding author. E-mail: zhenghu@nju.edu.cn

Figure S1. The schematic illustration of the experimental apparatus. The mixture precursor (0.5 g) of Ga, Ga₂O₃ powder and red phosphorus was placed at the upstream end of a small quartz tube. About 0.1 g AlN nanowires were put at the downstream end of the small quartz tube as the reducer. In our comparison experiments, AlN nanowires were also substituted by AlN nanoparticles, γ -Al₂O₃ or Fe-Co/ γ -Al₂O₃ powders respectively. After synthesis, the products both at upstream and downstream regions were collected respectively for characterization.

Figure S2. TEM image of the used reducer of AlN nanowires. The AlN nanowires were prepared via an extended VLS growth process [Q. Wu et al., J. Mater. Chem. 2003, 13, 2024.]. Briefly, 1 g aluminum powder (99.9 %, 100-200 mesh) was dispersed into the aqueous solution of MgSO_4 . After water was vaporized at ambient temperature, the mixture was further dried at 100°C for 5 h to obtain a MgSO_4 -loaded Al powder (1.0 mmol MgSO_4 per gram of Al), which was then placed into a horizontal tubular furnace, evacuated and flushed with Ar for several times to remove oxygen and moisture. After that, the furnace was heated at a rate of $15^\circ\text{C}/\text{min}$ under flowing Ar of 100 sccm. When the temperature reached 850°C , the flowing gas was switched to NH_3/N_2 of 300 sccm, and the furnace was continually heated up to 1100°C and maintained at this temperature for 1 h. Then the furnace was cooled down to ambient temperature under flowing NH_3/N_2 and the AlN nanowires with the diameters of about 15 nm were obtained.

Figure S3. EDX spectra corresponding to the marked locations (squares) in the product. The elements are marked above the corresponding peaks. (a) EDX spectrum from the side wall of the GaP nanotube. In addition to the Ga and P peaks for GaP nanotubes, the signals for Al and O come from the Al_2O_3 amorphous layer on the surface of the GaP nanotubes which is highlighted by the arrow in the corresponding HRTEM image underneath. The Al_2O_3 species was the

by-product, which was simultaneously formed and mixed with the Ga droplet. [see main text: $3\text{Ga}_2\text{O}(g) + 2\text{AlN}(s) \rightarrow \text{Al}_2\text{O}_3(s) + 6\text{Ga}(l) + \text{N}_2(g)$]. With the growth of the GaP nanotubes out from the Ga droplet, partial Al_2O_3 species was transferred onto the surface of the GaP nanotubes. The signals for Cu and Mg come from the TEM grid and the contamination of Mg-containing reducer of AlN nanowires, respectively. (b) EDX spectrum from the ‘ingredient supplier’ attached to the end of the GaP nanotube. It is seen that the ‘ingredient supplier’ is mainly composed of Ga element. As mentioned in (a), the signals for Al and O come from the Al_2O_3 by-product. (c) EDX spectrum from the filled part of the GaP nanotube. It is seen that the filled ‘grey’ substance was GaP, otherwise the relative peak intensity of Ga to P should be much larger.

In a word, partial Al_2O_3 by-product was coated on the unconsumed AlN nanowires. The rest was mixed within the Ga droplets which was partially transferred onto the surface of the GaP nanotubes during their growth. It is worth noting that the diffraction peaks for the Al_2O_3 by-product could not be detected in the XRD pattern (see Figure 2 in the main text), indicating the low concentration, high dispersion and amorphism of the alumina species.

Figure S4. (a) Typical TEM image of the GaP nanotube partially filled by 'dark' substance. (b) HRTEM image corresponding to the filled part in (a). The core-shell structure is clearly illuminated.

Figure S5. Typical TEM images of the products synthesized by substituting AlN nanowires with (a) AlN nanoparticles, (b) γ -Al₂O₃, and (c) Fe-Co/ γ -Al₂O₃. In (a), GaP nanotubes could still be observed, which indicates that the formation of GaP nanotubes did not depend on the shape of the AlN reducer. In (b) and (c), no GaP nanotubes but particles could be observed (in combination with Figure S6), indicating the importance of the AlN reducer.

Figure S6. XRD pattern corresponding to the product in Figure S5b. The peaks highlighted by arrows indicate that GaP was formed in the product. Other peaks come from the γ - Al_2O_3 support.

Figure S7. Typical TEM image of the mixture product in the region for putting the mixture of Ga, Ga_2O_3 and P precursors at the upstream part of the small quartz reaction tube. No GaP nanotubes but particles could be observed although Ga and P existed there. This is because that the granular Ga precursor is too big to reach the supersaturated level necessary for nanotubular precipitation.

Figure S8. Typical TEM images of the product when red phosphorous precursor was excessively used (The mole ratio of Ga:Ga₂O₃:P is 4:1:12). GaP nanowires rather than nanotubes were observed.

S9 Brief analysis on the Raman and photoluminescence spectra of the product

The Raman and photoluminescence spectra (Figure 4 in the main text) came from the mixture of GaP, Al₂O₃ and AlN. But they could still reflect the optical properties of the GaP nanotubes.

Actually we measured the Raman spectrum in the range of 200-1000 cm⁻¹ as shown below (a). It is seen that only phonon modes for GaP appeared. The modes for AlN nanowires, which should be mainly in the range of 600-700 cm⁻¹, have not been observed. The possible reason is that the unconsumed AlN nanowires were coated by a thick layer of Al₂O₃ by-product [Al₂O₃ species produced through the reaction of “3Ga₂O (g) + 2AlN (s) → Al₂O₃ (s) + 6Ga (l) + N₂ (g)” should be easily adhered on the surface of the unconsumed AlN nanowires]. The shielding effect of the thick layer of Al₂O₃ made the Raman signals for AlN undetectable. In addition, the GaP nanotubes and the unconsumed AlN nanowires are just physically mixed together. The influence of the AlN on the Raman spectrum of the GaP should be negligible. Hence, in the manuscript we have only provided the Raman spectrum in the range of 250-500 cm⁻¹ for GaP for clarity (Figure 4a). The surface Al₂O₃ species could slightly influence the Raman modes of the GaP nanotubes, which has been discussed with reference to some literatures (Page 5, Line 5~12). We also measured the Raman spectrum of the original AlN reducer, which is shown below (b) for your reference.

It is known the photoluminescence emission of AlN nanowires is centered at about 2.84 eV with the excitation energy of 4.28 eV. This emission originated from the surface impurities and defects.¹ In this study, for the photoluminescence spectrum of our product, we used the excitation energy of 2.8 eV (442nm line of He-Cd laser), smaller than 2.84 eV for AlN. So the emission from the AlN nanowires would not occur and only the emission peak of GaP nanotubes could be observed. In addition, the GaP nanotubes and the unconsumed AlN nanowires are just physically mixed together. Hence the influence of the AlN on the photoluminescence spectrum of the GaP should be negligible. In comparison with that of bulk GaP, the emission peak of our GaP nanotubes shows a little bit red-shift, which may result from the surface Al₂O₃ impurity as discussed in Page 5, Line 15~19 in the manuscript.

(1) Xu, C. K.; Xue, L.; Yin, C. R.; Wang, G. H. *Phys. Stat. Sol. A* **2003**, 198, 329.