

# SYNTHESIS AND CHARACTERIZATION OF ULTRALONG Si<sub>3</sub>N<sub>4</sub> NANOBELTS WITH UNIQUE OPTICAL AND FLEXIBLE NANOMECHANICAL PROPERTIES

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**Keywords:** Si<sub>3</sub>N<sub>4</sub>, Nanobelts, Optical, Nanomechanical, Nanoindentation

## ABSTRACT

In this paper, several millimeters long Si<sub>3</sub>N<sub>4</sub> nanobelts (NBs) with a cross-section of 100-700 nm in width and 30-200 nm in thickness were successfully synthesized via an effective method with the raw materials of graphite, nanosilicon and nanosilica. Alumina-assisted vapor-liquid-solid (VLS) was proposed for the growth mode of ultra-long Si<sub>3</sub>N<sub>4</sub> NBs, in which alumina may be as a novel and highly effective mediator playing an important role in adjusting the content of reactive silicon during the growth of ultra-long Si<sub>3</sub>N<sub>4</sub> NBs. The room-temperature photoluminescence (PL) spectrum showed that the synthesized  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> NBs had two strong emissions peaks centered at 551 nm (2.25 eV) and 697 nm (1.78 eV) located in the yellow and red spectral range, which can be explained by the size effect and presence of a small amount of Al, offering an effective method for preparing Si<sub>3</sub>N<sub>4</sub> nanomaterials with unique optical properties. In situ nanoindentation was used to probe the nanomechanical property of Si<sub>3</sub>N<sub>4</sub> NBs by a hybrid SEM/SPM system and the Young's modulus of a Si<sub>3</sub>N<sub>4</sub> NB with about 300 nm in width and 100 nm in thickness was approximately 483.78 GPa, suggesting much larger than those of bulk and film of the Si<sub>3</sub>N<sub>4</sub> materials, providing value and guidance for studying the properties of Si<sub>3</sub>N<sub>4</sub> nanomaterials and for expanding their possible applications.<sup>5</sup>

## 1 INTRODUCTION

Owing to their unique and excellent properties compared with their bulk counterparts, one-dimensional (1D) silicon nitride (Si<sub>3</sub>N<sub>4</sub>) nanomaterials (e.g., nanowires and nanobelts) have attracted considerable attention due to their potential applications in widely fields with composites, nano- and micro- electronic, and nanoscale devices.<sup>1</sup> Numerous techniques, including the pyrolysis of polymeric precursors, carbothermal reduction and chemical vapor deposition (CVD), are applied to synthesis 1-D Si<sub>3</sub>N<sub>4</sub> nanomaterials.<sup>2</sup> Moreover, the lengths on the order of millimeters or even centimeters long Si<sub>3</sub>N<sub>4</sub> nanomaterials might be more valuable compared to short ones in some fields (e.g., connections for devices and reinforcements for composites).<sup>3</sup> Inspired by this, some literatures have been reported about the preparation of high-yield and ultra-long Si<sub>3</sub>N<sub>4</sub> nanomaterials according to our survey.<sup>4</sup> It is worth noting that an accurate measurement of the nanomechanical properties of 1D Si<sub>3</sub>N<sub>4</sub>

nanomaterials is of critical importance before they are applied in all of the above applications. Scanning probe microscopy (SPM) has proven to be a valuable device for manipulating and characterizing the properties of individual nanostructures through techniques such as nanoindentation, three-point bending and tensile tests. However, to the best of our knowledge there has not been a report of the nanomechanical properties of  $\text{Si}_3\text{N}_4$  nanowires (NWs) by an SPM/SEM system up to now.<sup>5</sup>

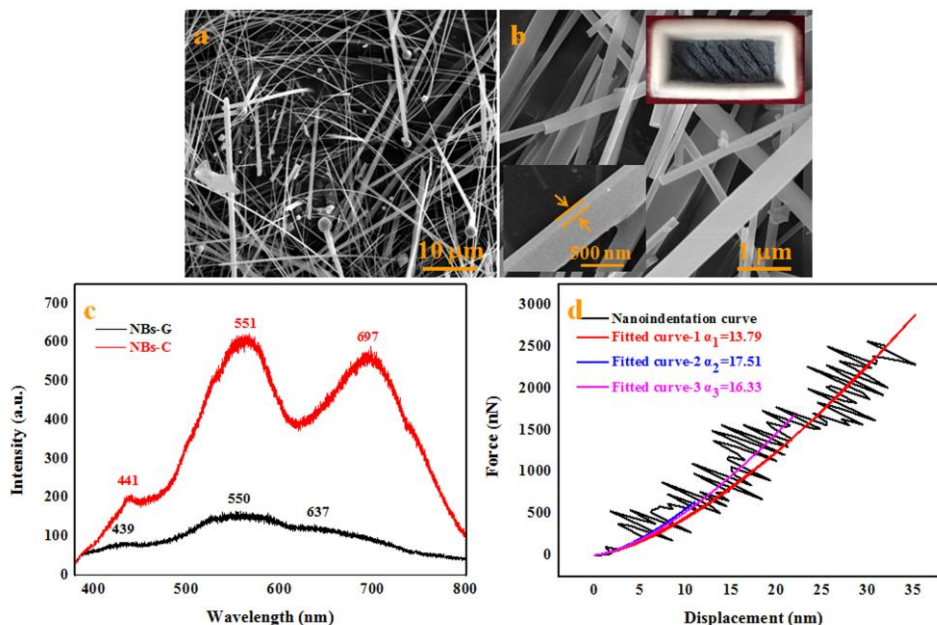


Figure 1: (a)-(b) SEM images of the as-prepared white wools obtained on the inner wall of ceramic crucible. Inset: the macroscopic morphology of the achieved products. (c) PL spectra of  $\alpha$ - $\text{Si}_3\text{N}_4$  NBs obtained on the inner walls of ceramic crucible (red line marked as NBs-C) and on the inner walls of graphite crucible (black line marked as NBs-G) under excitation of a 325 nm He-Cd laser at room temperature. (d) A typical force-displacement curve extracted from nanoindentation experiments with different fitted curves as displacement increases.<sup>5</sup>

## 2 CONCLUSIONS

Ultra-long  $\text{Si}_3\text{N}_4$  NBs with several millimeters long were successfully prepared by a low-cost method with simple raw materials. Alumina-assisted VLS mechanism was used to disclose the growth process of  $\text{Si}_3\text{N}_4$  NBs obtained on the inner walls of the crucible with a cross-section of 100-700 nm in width and 30-200 nm in thickness, in which alumina might play an important role in the growth of ultra-long  $\text{Si}_3\text{N}_4$  NBs. The PL spectrum of  $\alpha$ - $\text{Si}_3\text{N}_4$  NBs at room temperature showed two strong emission peaks located at 551 nm (2.25 eV) and 697 nm (1.78 eV), in which a possible emission mechanism was also proposed with a larger size and a small amount of Al. The Young's modulus of  $\text{Si}_3\text{N}_4$  NBs with an average value of 483.78 GPa was comparable to the values reported in the literature suggesting that this method not only provides an effective way to synthesis ultra-long  $\text{Si}_3\text{N}_4$  NBs on an industrial scale, but also supplies significance guidance in the studies of the mechanical properties and the applications of  $\text{Si}_3\text{N}_4$  nanomaterials.<sup>5</sup>

## ACKNOWLEDGEMENTS

This work was supported by the National Science Foundation (51202048, 51372047, 11402252, 11421091, 91216301 and 51525201) of China, and National Key Laboratory of Science and

Technology on Advanced Composites in Special Environments, KL.PYJH.2016.001. The authors gratefully acknowledge the support of Dr. Ma and Prof. Zhang from Beijing University of Technology in the nanomechanical testing and characterization of Si<sub>3</sub>N<sub>4</sub> NBs.<sup>5</sup>

## REFERENCES

- [1] G. Gundiah, G. V. Madhav, A. Govindaraj, M. M. Seikh and C. N. R. Rao, Synthesis and characterization of silicon carbide, silicon oxynitride and silicon nitride nanowires, *Journal of Materials Chemistry*, **12**, 2002, pp. 1606-1611 (doi: [10.1039/B200161F](https://doi.org/10.1039/B200161F))
- [2] W. Yang, H. Wang, S. Liu, Z. Xie and L. An, Controlled Al-doped single-crystalline silicon nitride nanowires synthesized via pyrolysis of polymer precursors, *The Journal of Physical Chemistry B*, **111**, 2007, pp. 4156-4160 (doi: [10.1021/jp070642+](https://doi.org/10.1021/jp070642+))
- [3] S. Chaturvedi and P. N. Dave, Design process for nanomaterials, *Journal of Materials Science*, **48**, 2013, pp. 3605-3622 (doi: [10.1007/s10853-013-7196-x](https://doi.org/10.1007/s10853-013-7196-x))
- [4] F. Gao, W. Yang, Y. Fan and L. An, Aligned ultra-long single-crystalline  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> nanowires, *Nanotechnology*, **19**, 2008, pp. 105602 (doi: <http://dx.doi.org/10.1088/0957-4484/19/10/105602>)
- [5] S. Dong, P. Hu, X. Zhang, Y. Cheng, D. Zhang, L. Yan and G. Chen, Size dependence of optical and mechanical properties of Si<sub>3</sub>N<sub>4</sub> nanobelts controlled by flow rates, *Journal of Materials Chemistry C*, **4**, 2016, pp. 11212-11218 (doi: [10.1039/C6TC03802F](https://doi.org/10.1039/C6TC03802F))