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# Ultra-long $Si_3N_4$ nanobelts prepared by nanosilicon, nanosilica and graphite

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ABSTRACT

The composition and morphology of obtained products depended on the processing atmosphere using the raw materials of nanosilicon, nanosilica and graphite, with $N_2$-generating several millimeters long single-crystal $Si_3N_4$ nanobelts (NBs) and Ar SiC nanobelts. The width and thickness of in situ NBs ranged from 100 to 300 nm and 50–100 nm with an average width of 196 nm, while the width and thickness of ex situ NBs fluctuated from 150 to 500 nm and 80–200 nm with an average width of 436 nm. Alumina-assisted VS mechanism was proposed for the growth mode of in situ growth of $Si_3N_4$ nanobelts, while a combined mechanism involving VS and VLS was controlled the growth of $Si_3N_4$ nanobelts obtained on the inner walls of the crucible due to the presence of $Fe_2O_3$, which provides an effective means of fabricating ultra-long $Si_3N_4$ nanobelts on an industrial scale.



## 1. Introduction

Recently, one-dimensional (1D) nanostructures have attracted tremendous attention due to their potential application for promoting the fundamental researches and for constructing nanocomposites and nanoelectronics devices [1–4]. The properties of nanostructures not only rely on their chemical composition but also on their morphology, such as microstructure, phase and size [5]. Owing to their unique morphologies with rectangle–like cross section, belt-like nanostructures could be used as a possible candidate material for nanodevices, which have been prepared through different chemical or physical routes [6]. $Si_3N_4$ is an important material for a number of applications because of its unique mechanical, optical and electronic properties, such as high dielectric constant, large electronic gap, and strong resistance against thermal shock [7–9]. Great efforts have been made to synthesize $Si_3N_4$ nanobelts with numerous methods, including pyrolysis of polymeric precursor, solvothermal synthesis, sol–gel method, chemical vapor deposition, and carbothermal reduction [10–12]. For example, Yang et al. obtained $Si_3N_4$ nanomaterials with the lengths up to several millimeters through $FeCl_2$-catalyzed pyrolysis of a polysilazane precursor and ultra-long $Si_3N_4$ NBs were also successfully synthesized by Al-catalyzed pyrolysis of amorphous silicon carbonitride precursors [13,14]. Although high-yield and ultra-long $Si_3N_4$ NBs were obtained by these techniques, several shortcomings could be listed as following sentences. For instance, much residual carbon usually remained in the final products during the method of pyrolysis of polymeric precursor, and severe demands of materials and equipments, such as inflammable gas and superatmospheric pressure, which hinder the further separation and application of $Si_3N_4$ nanomaterials [15]. Furthermore, the lengths on the order of millimeters or even centimeters long $Si_3N_4$ nanomaterials might be more valuable compared to short ones in some fields (e.g., connections for devices and reinforcements for composites) [16]. Inspired by this, other novel preparation approaches should be explored to prepare high-yield and ultra-long $Si_3N_4$ nanomaterials.

In this paper, we attempt to synthesis of several millimeters long nanomaterials just by inorganic powders with nanosilicon, nanosilica and graphite under the conditions of Ar and $N_2$, respectively. The obtained nanostructures were characterized detailed by many methods, and effect of different atmosphere on the nanostructures was investigated, including flow rates. Moreover, the possible growth mechanisms for the obtained nanomaterials were also proposed, respectively.

## 2. Experimental

### 2.1. Preparation of ultra-long nanomaterials

Commercial available nanosilicon (100 nm, Hefei Kaier Nanometer Energy & Technology Co., Ltd, China), nanosilica (25 nm, Aladdin Industrial Corporation) and the graphite flake (20 μm,

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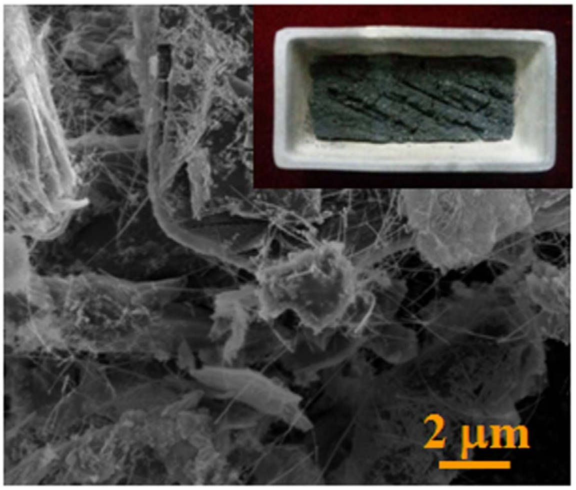


**Fig. 1.** SEM image of products obtained on the surface of mixture powder at 1500 °C in 100 ml/min of Ar with macroscopic morphology.

Qingdao Tiansheng Graphite Co., Ltd, China) were used as raw materials to synthesize several millimeters long $Si_3N_4$ nanomaterials. A detailed synthesis process was described and the powder was mixed as follows: 13.92 wt% nanosilicon, 29.83 wt% nanosilica and 56.25 wt% graphite flake. The mixture powder was ball-milled in ethanol for 6h with SiC balls and dried in a rotating evaporator, and then the mixture powder (1 g) was put into a ceramic crucible (60 mm × 30 mm × 30 mm) and the crucible was placed into a tube corundum furnace. The furnace was heated up from room temperature to 300 °C with 80 min and kept for 10 min, and then heated up to 800 °C with 120 min and kept for 10 min, and further heated up to 1500 °C with 230 min and kept for 2 h. The furnace was cooled to 500 °C firstly with 300 min and then naturally cooled to room temperature after the heating was terminated. High-purity argon or nitrogen gas was kept flowing during the experimental process. The products looked like white wools were found on the surface of mixture powder and on the inner walls of crucible.

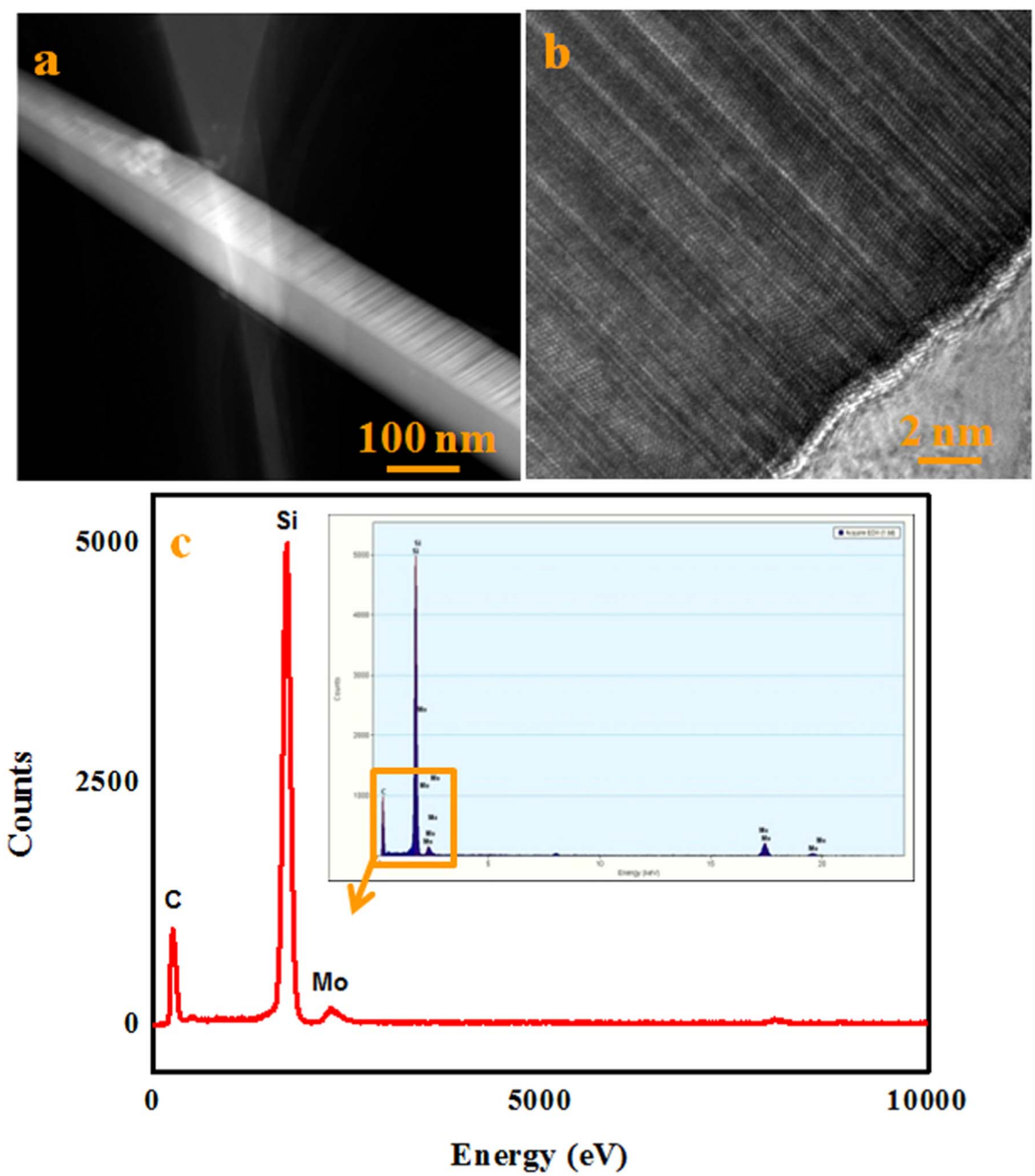


**Fig. 2.** STEM and HRTEM images, and EDS spectrum of the stem of products obtained on the surface of mixture powder at 1500 °C in 100 ml/min of Ar. (a) STEM image, (b) HRTEM image, and (c) EDS spectrum of the stem of obtained nanomaterials.