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# KINETICS STUDY AND ONLINE MONITORING OF *IN-SITU* GROWTH OF ZINC-OXIDE NANOWIRE ARRAYS WITHIN MICROFLUIDIC CHAMBERS

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## ABSTRACT

We present online monitoring of nanowires growth within a microfluidic chamber. This achievement is introduced for the first time thanks to simple and non-invasive real-time optical method, where the results were confirmed later by scanning electron microscopy (SEM). Nanowire length and diameter could be monitored versus growth time thanks to remote optical measurement. In this work, we also report kinetics study and online monitoring of *in-situ* growth of Zinc-Oxide nanowires (ZnO-NWs) within a microfluidic chamber showing the impact of different growth parameters on the NWs characteristics. It appeared that growth within a microfluidic reactor provides 4-times faster growth rate compared to macroscopic growth due to the confined environment of the chemical reaction. It also appears that varying the flow rate has more influence on the NWs diameter rather than the NWs length.

## KEYWORDS

Real-time monitoring, Microfluidic environment, Zinc-oxide nanowires, *in-situ* hydrothermal growth, Optical characterization, Effective refractive index, UV-vis-NIR spectroscopy.

## INTRODUCTION

Zinc-Oxide nanowires (ZnO-NWs) are multifunctional materials attracting increased interest due to their numerous excellent intrinsic properties. Thus, various efforts were devoted in the synthesis of the ZnO-NWs and it have been utilized in versatile applications such as biophotonic sensor [1], nanogenerator of electricity [2] and water purification [3]. In this work, we used the easy and low-cost hydrothermal method for the ZnO-NW growth [4].

Microfluidic devices also show increased interest over conventionally sized system due to reduction of sample volume consumption, faster reaction in microscale and cost reduction. The integration of functional nanostructures within microfluidic devices can synergize the advantages of both unique properties of nanomaterials and diverse functionalities of microfluidics. Some efforts were devoted in literature taking advantage of the microfluidic environment to grow the ZnO-NWs *in-situ* within microchannels whose width did not exceed 500  $\mu\text{m}$  [5], [6]. A combination between conventional and *in-situ* growth was reported in ref [7] and recently in ref [8] they succeeded obtaining nanostructures within capillary tubes. In this work, we report kinetics study on *in-situ* growth of the ZnO-NWs on wider microchambers showing the effect of different growth parameters on the NWs characteristics

including nanowire length and diameter. In addition, we present online monitoring of the NWs length during the growth non-invasively without growth interruption.

## MATERIALS AND METHODS

The microfluidic chamber consists of silicon base containing the ZnO seed layer bonded to PDMS molded by soft lithography. The chamber size is 10 mm x 10 mm and 100  $\mu\text{m}$  height where a photography image of the fabricated chamber is shown in Figure 1. 4-branching level biomimetic flow distribution tree [9] is designed as input and output stages for the chamber to ensure uniform flow of the growth solution and uniform NWs growth over the wide chamber.

Figure 2 shows the growth setup, also used later for real-time monitoring. Monitoring was done non-invasively using optical fiber reflection probe above the PDMS illuminating the sample perpendicularly and collecting reflected light and delivering it to the UV-vis-NIR spectrometer.



Figure 1: Photography of the microfluidic growth chip showing the wide growth chamber and the flow distribution trees.

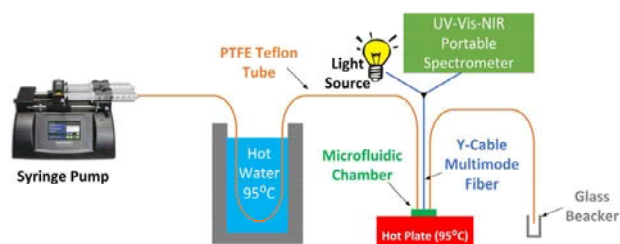


Figure 2: Schematic of the ZnO-NWs *in-situ* growth setup and the online time monitoring.

## EXPERIMENTAL RESULTS

### Kinetics of ZnO-NWs growth within microfluidic chambers

In this first part of the study we conducted a set of experiments of growth of ZnO-NWs within microfluidic chambers, where we varied the growth time and the flow rate. Upon completion of the growth, each micro-chamber was cut so as to proceed with observations on scanning electron microscopy (SEM) so as to retrieve the NWs characteristics.

Good quality and well-oriented ZnO-NWs are grown uniformly on the whole chamber thanks to the flow distribution tree. Different growth parameters have been tested to achieve the best conditions for the *in-situ* growth as shown in the SEM images in Figure 3 showing the growth time effect (a) and the flow rate effect (b). Increasing the growth time increases the NWs size as shown from the SEM images in Figure 3 (a) following a similar trend as for the macroscale conventional growth [10]. Microfluidics environment provides a fast but efficient way to produce large scale ZnO-NWs with 4-time faster growth rate in comparison to macroscale growth as shown in Figure 4 (a) and (b), respectively. Figure 5 summarizes the achieved NWs length and diameter versus flow rate. Increasing the flow rate has more significance on increasing the diameter rather than the length as the NWs can be seen as a layer-by-layer growth, where higher flow rate involves a spread on the NW size.

### Non-invasive real time monitoring of ZnO-NWs growth within a microfluidic chamber

In this second part of the study, we conducted another experiment, where there was no need to destroy the microfluidic chambers so as to retrieve the nanowires characteristics. We were even able to proceed with online monitoring of the NW growth within the microfluidic chamber in a completely non-destructive manner.

This result is achieved based on the acquired spectra every 6 minutes as shown in Figure 6 demonstrating the evolution of the NW growth. The NW length is extracted from the interference pattern following similar procedure to our work presenting the spectral domain attenuated reflectometry (SDAR) in ref [11]. The process of retrieving the NW thickness and filling ratio values makes use of the interference pattern contrast and the spectral periodicity in the reflection response which involve a best fit of the measured spectra with simple theoretical modeling based on the effective medium approach. A summary of the achieved lengths with time is presented in Table 1 and the final NWs length is confirmed using SEM as a reference method showing very good agreement with the monitored length.

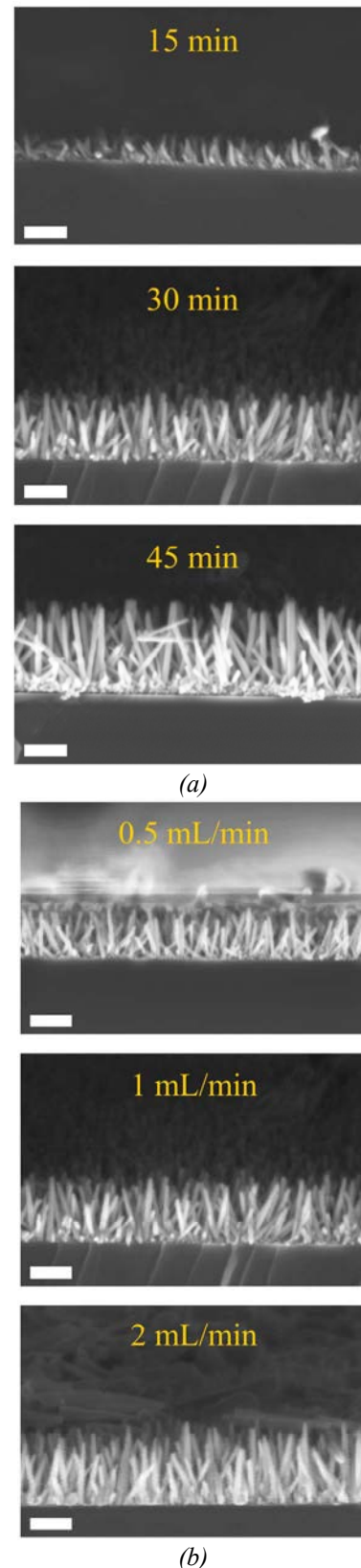


Figure 3: Cross-sectional SEM images showing: (a) The effect of the growth time on the NWs growth where the flow rate was fixed to 1 mL/min (b) The effect of the flow rate on the NWs growth where the growth time was fixed to 30-min. (Scale bar: 200 nm)

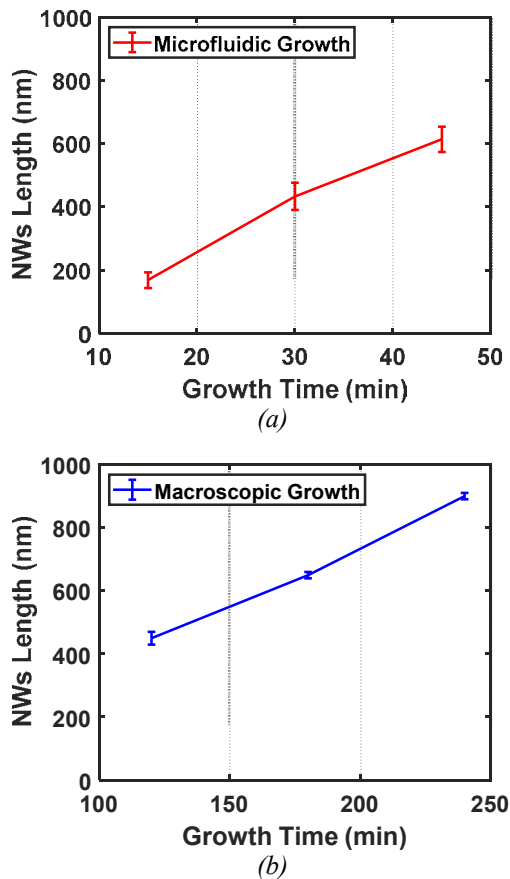


Figure 4: Comparison between the ZnO-NWs length achieved in (a) microfluidics and (b) conventional in macroscopic scale.

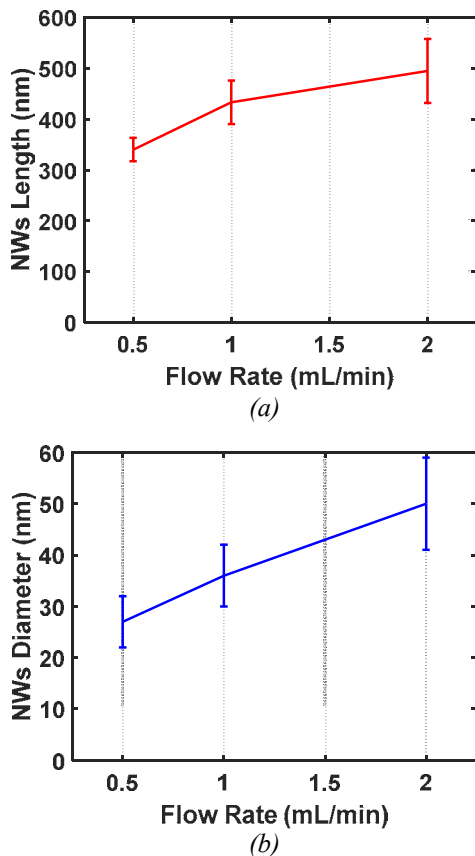


Figure 5: ZnO-NWs (a) Length and (b) Diameter versus flow rate.

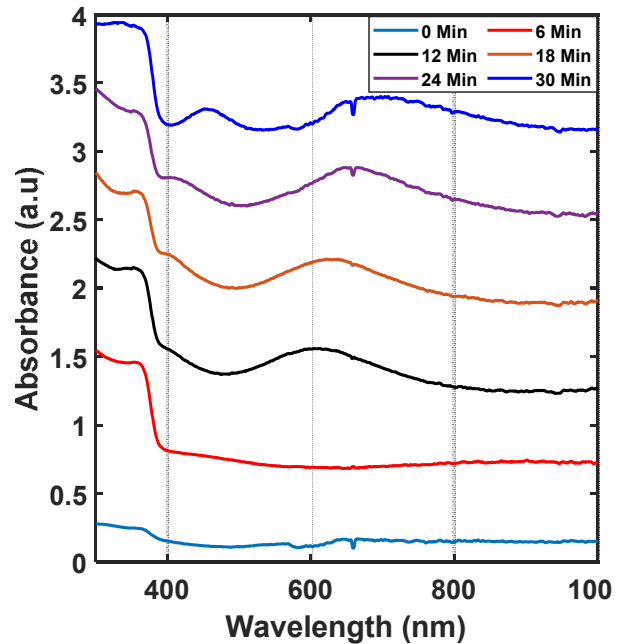


Figure 6: Online monitoring of the ZnO-NWs growth using UV-vis-NIR spectroscopy. The NWs length is retrieved making use of the interference pattern in vis-NIR range.

Table 1: Retrieved NWs length from optical online monitoring of ZnO-NWs growth at different time points during the growth.

Time (min)	Retrieved NWs Length (nm)
0	-
6	-
12	302
18	380
24	425
30	452
SEM (after growth)	472 ± 30

## CONCLUSION

In this work, taking advantage of the microfluidic environment, we reported kinetics study of *in-situ* growth of ZnO-NWs within a microfluidic chamber showing the impact of different growth parameters as the growth time and the flow rate on the NWs characteristics. In this case, getting the NWs length and diameters required SEM observation after irreversible cutting of the micro-reactors.

Furthermore, in the second part we successfully demonstrated, for the first time, non-invasive real time monitoring of the NWs length during the growth within the microfluidic chamber without growth interruption, thanks to remote acquisition of optical spectra and subsequent fast processing.

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