INTEGRATED HEATING AND COOLING MULTI-ZONE SILICON MICROREACTOR (MZSM) FOR INCREASED MONODISPERSITY IN TiO_2 NANOPARTICLE SYNTHESIS

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ABSTRACT

This paper discusses the first demonstration of both thermally isolated heated and cooled zones integrated into one Multi-Zone Silicon Microreactor (MZSM) to increase monodispersity in the production of TiO_2 nanoparticles. The novel thermal management scheme enables very sharp heating step function when initiating particle nucleation and immediate quenching of any further growth once the particles leave the growth region. As an early demonstration of the versatility of the novel MZSM, we have synthesized TiO_2 nanoparticles using a heated zone for growth kept at 100˚C and cooled zone held at room temperature. We have also shown the separation of nucleation and growth processes for the first time by first increasing the temperature to 200˚C for a short time and later decreasing the temperature to 70˚C for growth. The size distribution from the MZSM was compared to those synthesized by batch techniques [1] or other droplet flow reactors [2]. As an early demonstration of the versatility of the novel MZSM, we have successfully increased the monodispersity of TiO_2 nanoparticles

KEYWORDS

Microreactor, Nanoparticle, Microfluidics, TiO_2, Monodispersity, Thermal Isolation

INTRODUCTION

Research on microreactors aims to improve the quality of nanoparticle synthesis in order to obtain monodisperse size and shape distributions. In comparison to batch-wise synthesis techniques, microfluidic technology provides precise control on reaction conditions such as temperature and reagent concentrations [3].

In this paper we introduce a silicon-substrate microreactor that has thermally isolated heated and cooled zones for controlled synthesis of TiO_2 nanoparticles. Temperature of the reagents can be increased rapidly and later decreased in order to quench reactions. There are three thermally isolated zones used for controlled growth and nucleation of nanoparticles. We have demonstrated the growth of nanoparticles at 90˚C as well as separation of nucleation and growth processes by first increasing the temperature to 200˚C and later growing the nuclei at 70˚C. The capability to separate nucleation and growth is the key to achieve monodispersity in nanoparticle synthesis and it is not possible with batch techniques.

DESIGN

The MZSM is fabricated on a silicon substrate and microchannels are encapsulated by Pyrex substrate anodically bonded to the top surface for high chemical resistance and handling of high temperature and pressure reactions. The schematic of the MZSM is shown in Figure 1.

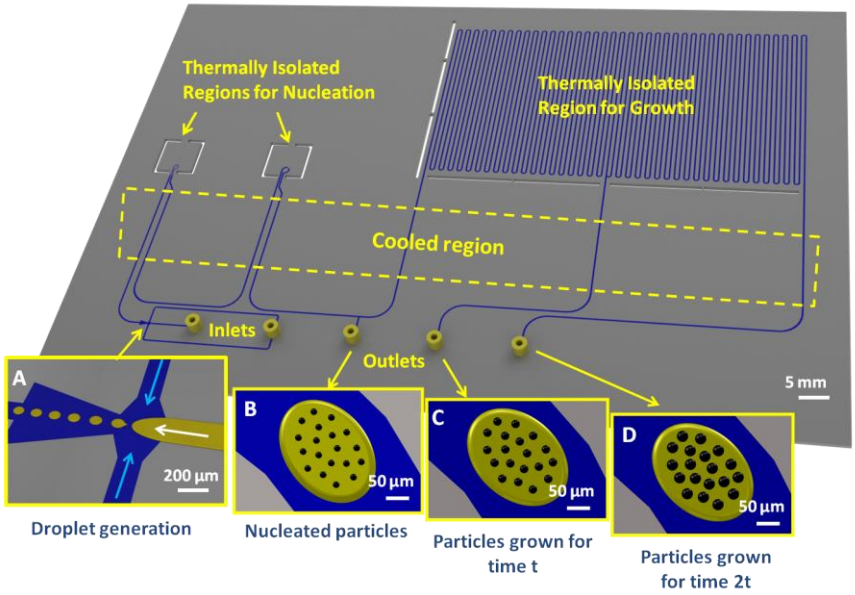

Figure 1. Schematic of the microreactor. There are three thermally isolated heated regions in the reactor for which the isolation is achieved by through etching of the Si substrate with an isolation gap of 0.5mm. Channels are 200 µm deep. A) Droplet generation. B-C-D) There are three outlets which gives the ability to observe particles at different stages.

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Droplets of reagents in an immiscible carrier fluid are generated by using triangular channel geometry to form uniform and stable droplets following the method in [4]. Two-phase flow provides uniform residence times in the heated regions and prevents contamination on channel walls. High temperature zones are heated by ceramic heaters attached to the bottom surface of the microreactor. The non heated regions are cooled by a chiller apparatus mounted to the surface through which water at 17˚C passes. Figure 2 shows the heating and cooling set-up of the microreactor. The temperatures at the heated and cooled regions are measured with an IR camera and a thermocouple embedded in the ceramic heaters attached to the substrate. Figure 3 shows an IR camera measurement when both nucleation and growth regions were heated. The goal of this figure is to show that we are able to achieve thermally isolated heated regions.

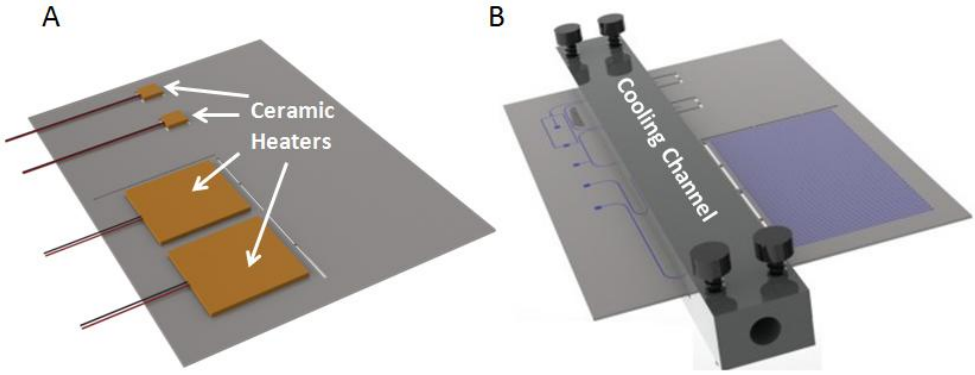

Figure 2. Heating and cooling elements of the microreactor. A) Heating is achieved by the attachment of ceramic heaters to the back side of the substrate. B) The non heated regions are cooled by a channel attached to the surface.

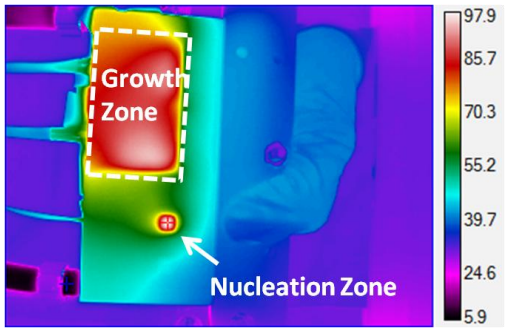

Figure 3. IR camera measurement of the heated and cooled zones.

EXPERIMENTAL RESULTS AND DISCUSSION

Two synthesis schemes for particle synthesis are possible with MZSM. Scheme 1, used for synthesizing the TiO_2 nanoparticles, utilizes the growth region and cooled region. Figure 4 shows real time images of nanoparticle synthesis inside the MZSM. The aqueous reagent was prepared by partially neutralizing $TiCl_3$ in HCl using NaOH (0.15M $TiCl_3$, 0.25M NaOH, pH 0.5) following the method in [1, 2]. Mineral oil with Span80 (2%wt) was used as the carrier phase. Particles were grown within the growth region of the microreactor for 240s. After the synthesis, particles were centrifuged in acetone and then dispersed in an aqueous solution of 4.9mM Na-oleate.

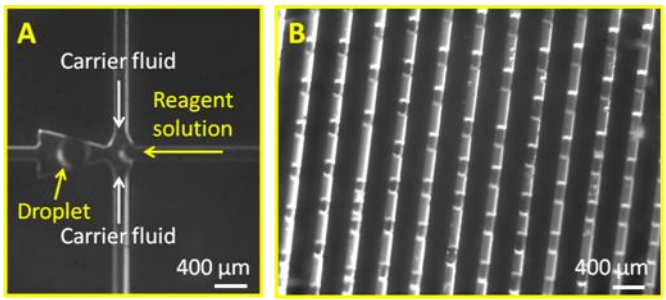

Figure 4. A) Stable droplet generation inside the microreactor. B) Droplets in the growth region. Flow rate of carrier fluid (mineral oil) is 1000µL/hr whereas flow rate of $TiCl_3$ solution is 500µL/hr.

TEM imaging shows that the average particle diameter is 26.5 ± 1.6 nm (Figure 5) with high yield. In Figure 5B, we can clearly see the Na-oleate coating on the particles. X-ray diffraction data in Figure 6 indicates that the particles were a combination of brookite and anatase TiO_2. Our results show that the controlled growth in the microreactor improved the monodispersity by 10% over previous methods.

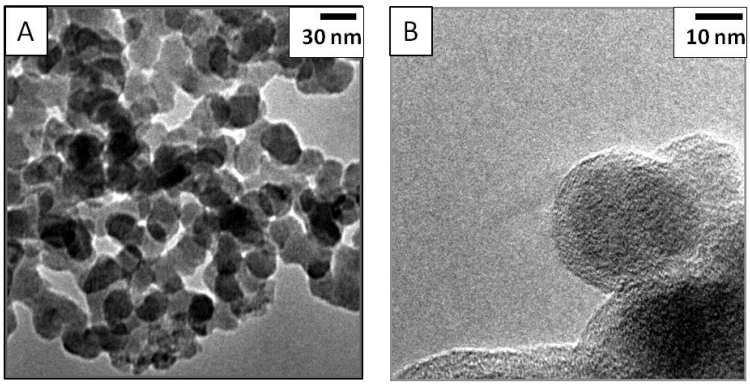

Figure 5. TEM images of TiO_2 nanoparticles grown in the microreactor. Figure B shows the Na-oleate coating around the particles. Particles are 26.5 ± 1.6nm in diameter.

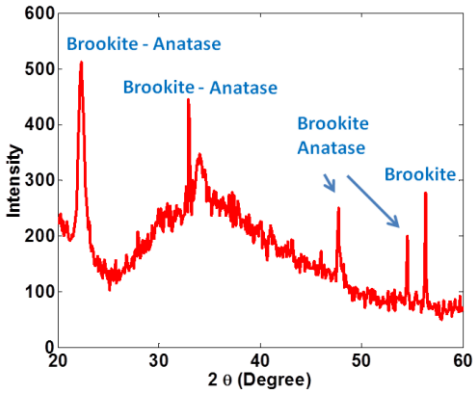

Figure 6. X-ray diffraction pattern of TiO_2 nanoparticles synthesized in the microreactor.

Scheme 2 adds in the regions for nucleation to separate the particle nucleation and growth processes. There are two thermally isolated heated regions for nucleation with short channels and different widths (100µm and 200µm). Separation of nucleation aims to nucleate particles at a high temperature for a short time without any growth. Only one nucleation zone is active for each synthesis. After nucleation, particles are heated at a lower temperature at the growth region without permitting for further nucleation. By this way particle monodispersity is aimed to be increased.

In order to demonstrate scheme 2, we synthesized TiO_2 nanoparticles by first nucleating them at 200˚C for 6 seconds. After nucleation, solutions travel through the growth region at a lower temperature of 70˚C for 120 seconds to allow particles to grow without further nucleation. The first demonstration of scheme 2 shows that the particle sizes were reduced to 5.2 ± 0.3nm in diameter. The reason for reduced sizes is nucleating a lot of particles at the beginning and leaving fewer reagents for growth in the later stage. If larger particles are desired, extra reagents can be provided from the third inlet of the device. The TEM images of the synthesized particles with separate nucleation and growth is shown in Figure 7.

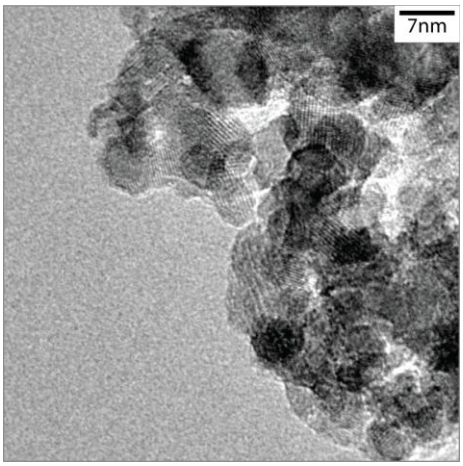

Figure 7. TEM image of nanoparticles synthesized with separated nucleation and growth. Crystal planes of nanoparticles can be observed very clearly. In this experiment, Na-oleate coating was not used.

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