

## Supporting Information

### Continuous Flow Synthesis of Phase Transition-Resistant Titania Microparticles with Tunable Morphologies

Zachary S. Campbell, Daniel Jackson, Jacob Lustik, Amur K. Al-Rashdi, Jeffrey A. Bennett, Fanxing Li, and Milad Abolhasani\*

Department of Chemical and Biomolecular Engineering  
North Carolina State University  
911 Partners Way, Raleigh, NC, United States 27695  
E-mail: [abolhasani@ncsu.edu](mailto:abolhasani@ncsu.edu)  
Webpage: [www.abolhasanilab.com](http://www.abolhasanilab.com)

#### S1. Supplemental Experimental Information

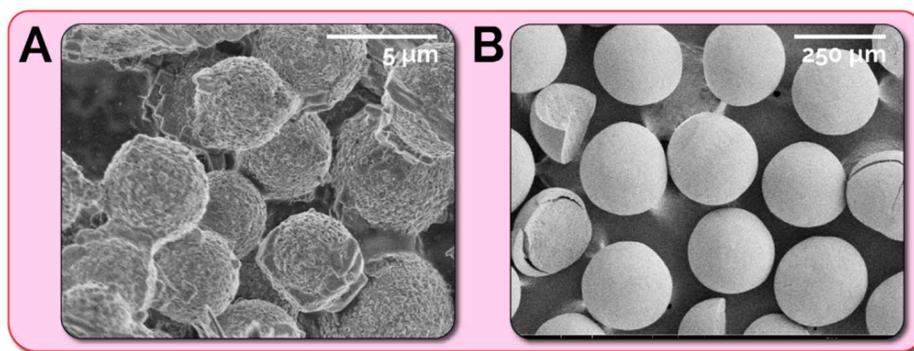
*Microreactor operation:* The dispersed phase and dyed toluene solutions were loaded into a syringe pump (Harvard Apparatus 33 DDS) using gas-tight glass syringes (SGE Analytical), while the continuous phase was loaded into two stainless steel syringes (Harvard Apparatus) placed in another syringe pump (Harvard Apparatus PHD 2000 Ultra). The microreactor was clamped in place vertically in front of an angled mirror (ThorLabs angled front-coated 50.8 mm mirror) placed under a microscope (Leica M205C) fitted with a high speed camera (FASTEC IL5). A high-power light source (Nathaniel Group Sugar CUBE Ultra LED illuminator) was used for high-speed bright-field imaging of the flow reactor with the microscope and camera during the reactor start-up and synthesis. A collimated UV LED (ThorLabs **M385LP1**) was clamped next to the exit capillary in a way that when it was turned on, it would only illuminate the reactor exit after the droplet formation zone. The microreactor and imaging setup were set up on a self-leveling optical table (ThorLabs PTS603) to minimize perturbations.

*Synthetic procedure:* The synthetic process was started by feeding the continuous phase and dyed toluene streams to the microreactor while purging air from the dispersed phase feed line. Once the air had been purged from the precursor feed line, the 4-way valve was switched so that the precursor was fed to the microreactor. Once stable flow was achieved with microdroplets of the desired size, the collimated UV LED was switched on, and a 100 mL collection vessel containing 50 mL of deionized (DI) water was placed under the exit capillary, with the capillary tip submerged in the collection solvent to prevent flow fluctuations due to dripping. Dispersed phase flow rates utilized for synthesis ranged from 0.5 to 80  $\mu\text{L min}^{-1}$ , while continuous phase flow rates ranged from 80 to 300  $\mu\text{L min}^{-1}$  (per syringe).

After collection, the microspheres were filtered using filter paper (Whatman 150 mm Grade 4) and a funnel, washed with DI water to remove the remaining formamide and Pluronic F108, and were dried at 90 °C for 3 h (Fisher Scientific IsoTemp Oven). Once dried, the microparticles were loaded into an alumina crucible (Columbia International 80x20x20 mm) and calcined for the desired time and temperature in a muffle furnace (MTI Corporation, KSL-1100X) with a 5 °C  $\text{min}^{-1}$  ramp rate.

## S2. Microparticle Size Variation

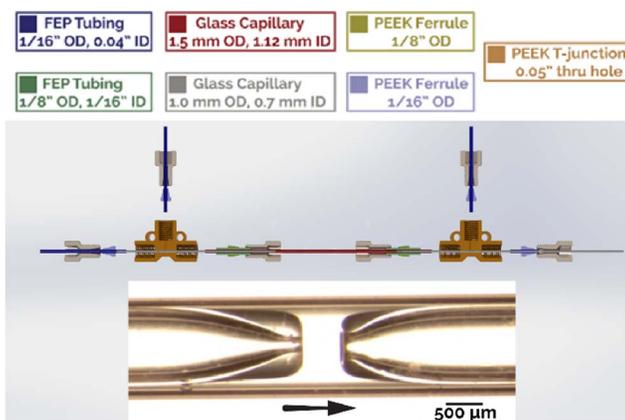
Using the microfluidic reactor, the smallest and largest microdroplets possible were synthesized using 30 wt% TBT-35 wt% ETPTA precursor. Both sets of particles were collected in formamide for consistency. **Figure S1A** shows the small particles synthesized using the UV integrated microreactor, which reach sizes  $<5\ \mu\text{m}$ . The small particles were not filtered or washed after collection as they were small enough that they could not be effectively filtered, even with quantitative filter paper. The particles were then moved from their collection vessel directly into a crucible, which was placed in an oven to evaporate the formamide. After evaporation, the microparticles were calcined at  $700\ ^\circ\text{C}$  to ensure that the residual formamide and Pluronic F108 were completely oxidized. **Figure S1B** shows the largest particles synthesized using the microreactor, which are  $\sim 250\ \mu\text{m}$  in diameter. The large particles were filtered and washed with water, dried for 3 h at  $90\ ^\circ\text{C}$ , and calcined at  $500\ ^\circ\text{C}$ .



**Figure S1.** The smallest and largest particles synthesized using the microfluidic reactor utilizing 30 wt% TBT- 35 wt% ETPTA. A) Small particles ( $\leq 5\ \mu\text{m}$ ) and B) large particles ( $\sim 250\ \mu\text{m}$ ).

## S3. Flow-Focusing Microreactor

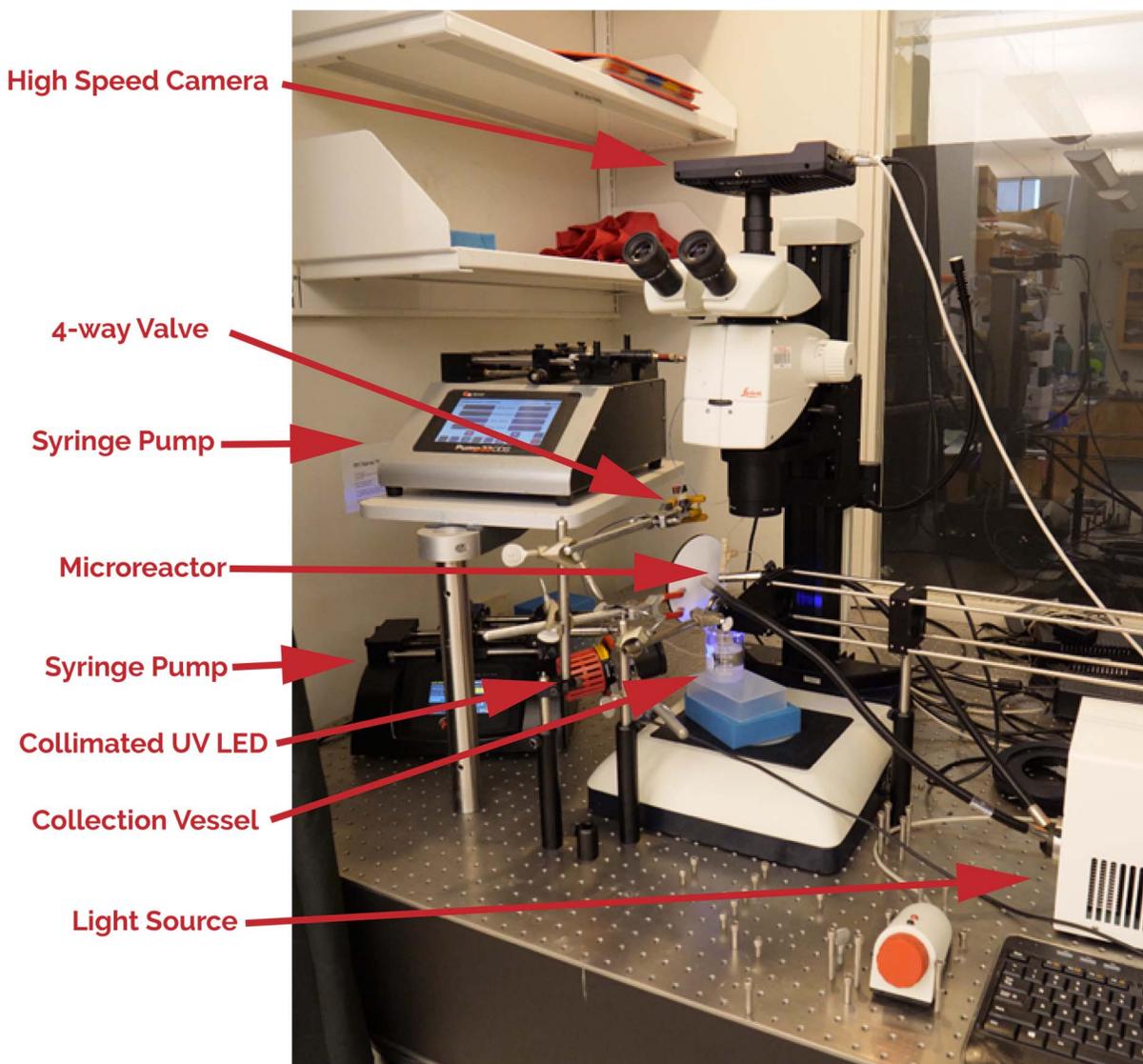
The flow-focusing microreactor was constructed according to **Figure S2**, with two constricted capillaries oriented tip-to-tip inside a larger capillary, resulting in an axisymmetric geometry with an inner inlet channel, an inner exit channel, and co/counter-flow annular inlets. The FEP tubing was attached to the PEEK/ETFE T-junctions with PEEK nuts and ferrules, while the inlet, exit, and external capillaries were given appropriately sized polymer sleeves prior to being attached with PEEK nuts and ferrules.



**Figure S2.** A deconstructed rendering of the microfluidic reactor assembly and image of the interior reactor geometry.

#### S4. Experimental Platform

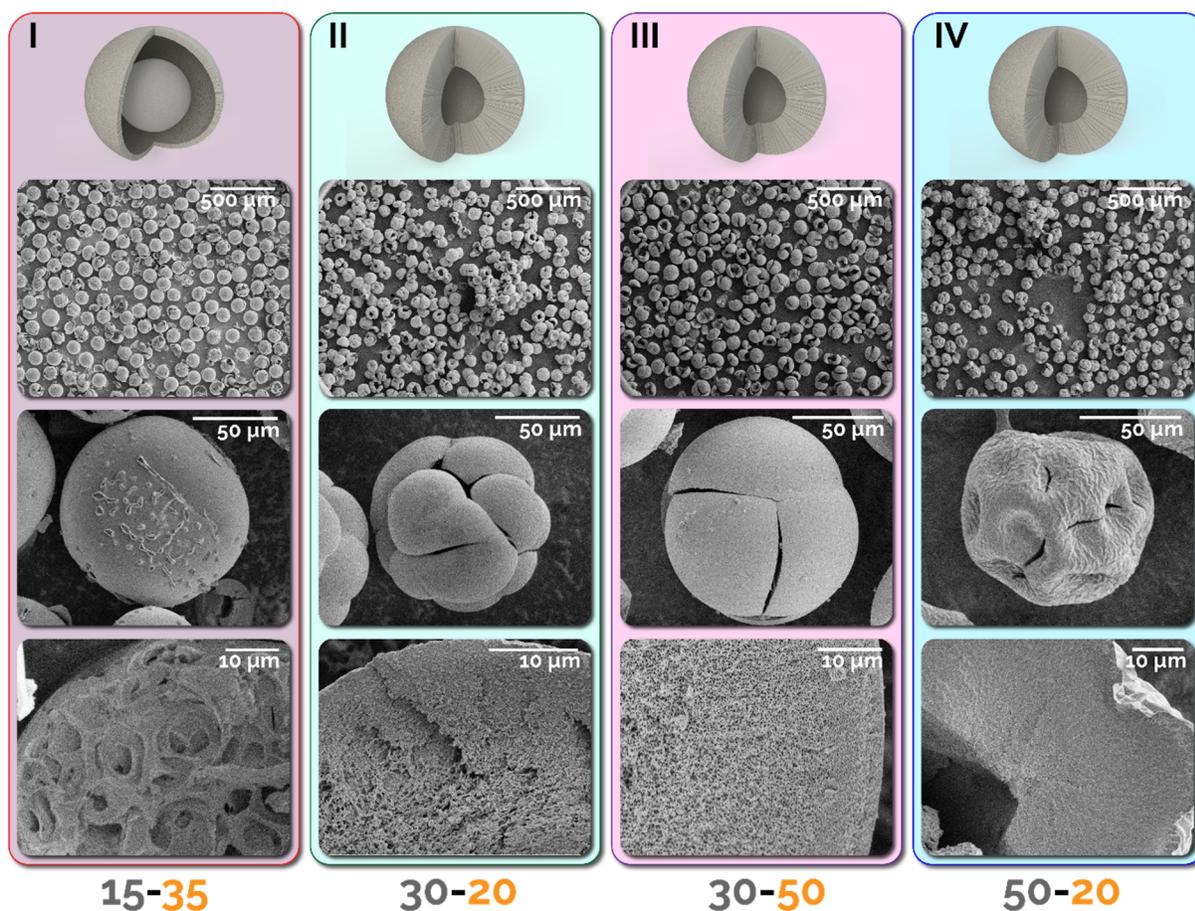
A collimated UV LED was integrated with the flow focusing microreactor to conduct in-line UV crosslinking of the photocurable polymer. The microreactor was clamped vertically in front of an angled mirror, which was positioned underneath a microscope fitted with a high-speed camera so that flow behavior inside the reactor could be monitored. In this configuration, the UV LED was clamped in place next to the microreactor, and was precisely oriented such that the exit capillary was illuminated, but no UV light was allowed to reach the droplet formation region of the microreactor.



*Figure S3. Picture of the microreactor setup integrated with collimated UV LED.*

## S5. Supplemental Particle SEM

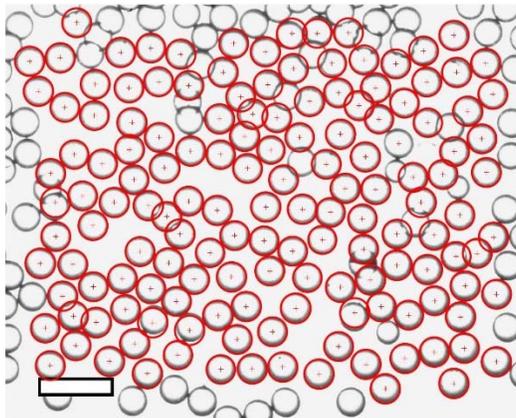
**Figure S4** presents wide field, single particle, and broken particle SEM images for the compositions not included in **Figure 2**. A yolk-shell morphology was observed for the 15-35 microparticles, while the 30-20, 30-50, and 50-20 microparticles were macroporous. Additional morphological differences were observed for the 30-20, 30-50, and 50-20 morphologies depending on the density of the ethoxylated trimethylolpropane triacrylate (ETPTA) network, with 30-20 and 50-20 samples resulting in “popcorn-like” or “raisin-like” morphologies, respectively, while the 30-50 sample resulted in a “fig-like” morphology. By comparison, the 30-35 microparticles presented in **Figure 2B IV** possess a spherical macroporous morphology. Thus, the less dense ETPTA networks result in microparticle deformation, moderately dense ETPTA networks result in spherical microparticles, and dense ETPTA networks cause particle rupture during calcination due to the quantity of ETPTA combusted.



**Figure S4.** Wide field, single particle, and broken particle SEM images of the remaining compositions not outlined in the main text. (I) Yolk-shell, 15 wt% TBT- 35 wt% ETPTA; (II) macroporous (popcorn-like), 30 wt% TBT-20 wt% ETPTA; (III) macroporous (fig-like), 30 wt% TBT-50 wt% ETPTA; (IV) macroporous (raisin-like), 50 wt% TBT-20 wt% ETPTA.

## S6. Microparticle Size Measurement

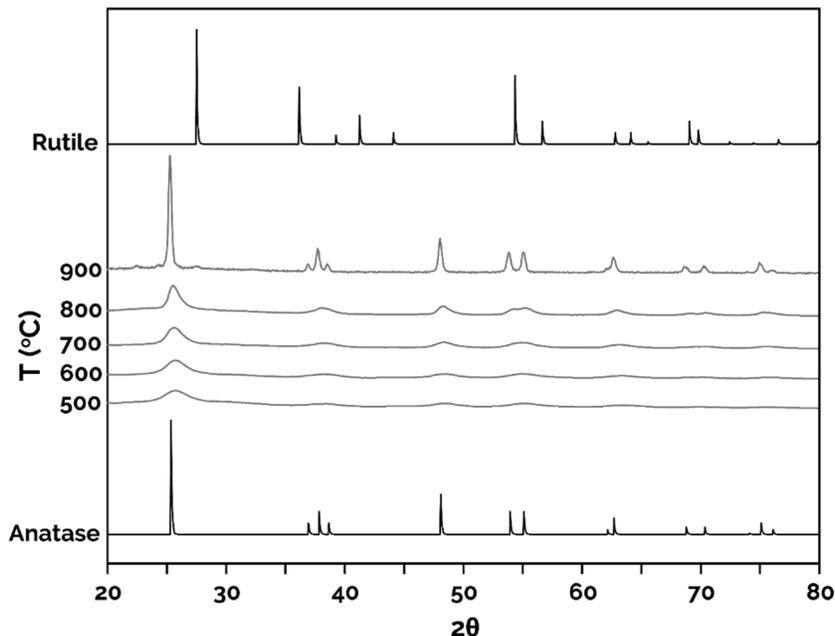
Automated image processing with custom-developed MATLAB image processing code was utilized to rapidly process and analyze post-collection microparticle diameters from bright-field images. Post-drying and post-calcination microparticle diameters were measured using ImageJ software.



**Figure S5.** Automated microparticle diameter measurement using a MATLAB-based image processing code. Scale bar is 500  $\mu\text{m}$ .

## S7. Structural Analysis of In-Flow Synthesized Titania Microparticles without Normalization

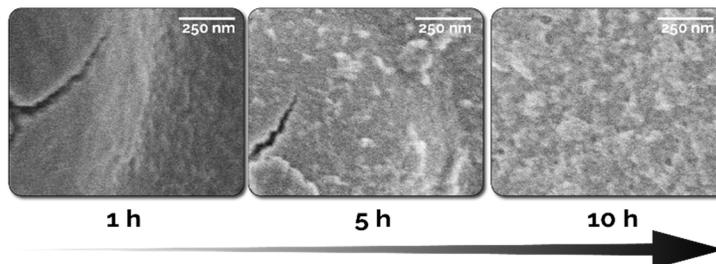
XRD spectra were collected for four microparticle samples synthesized with different precursor compositions. Each sample was calcined at 500°C for 1 h. The peak at  $2\theta = 25^\circ$  present in each spectrum is indicative of the anatase phase in each of the samples, while the absence of a peak at  $2\theta = 27^\circ$  indicates that no rutile is present.



**Figure S6.** XRD spectra of titania microparticles calcined at temperatures ranging from 500-900°C without normalization.

### S8. SEM Images of Particles Calcined at 500°C for 1, 5, and 10 h

Calcination time tests were conducted by calcining particles synthesized using precursor containing 15 wt% TBT and 50 wt% ETPTA at 500°C for 1, 5, and 10 h. The resulting microparticles were then characterized with SEM. Little difference was observed between the samples calcined at 1 h and 5 h, with some additional pores becoming visible after calcination for 10 h.



**Figure S7.** Surface SEM images of titania microparticles after calcination at (A) 1 h, (B) 5 h, and (C) 10 h.

### S9. Supplementary Videos

**Movie M1.** High resolution video of droplet formation in the microreactor. Precursor composition 15 wt% TBT- 35 wt% ETPTA. Camera frame rate 3286 fps.  $Q_D = 50 \mu\text{L min}^{-1}$ ,  $Q_C = 400 \mu\text{L min}^{-1}$  (200  $\mu\text{L min}^{-1}$  co-flow + 200  $\mu\text{L min}^{-1}$  counter-flow).