

Research Article

Continuous-Flow Synthesis of Thermochromic M-Phase VO₂ Particles via Rapid One-Step Hydrothermal Reaction: Effect of Mixers

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VO₂ particles are promising materials for thermochromic smart windows that reduce building energy loss. Continuous-flow hydrothermal processes showcase advantages for synthesizing VO₂ particles compared with traditional batch reaction systems. Mixers play a crucial role in particle fabrication in continuous-flow systems. In this study, a Center T-Mixer and a Collision Cross-Mixer are developed and implemented in a hot water fluidized suspension reaction (HWFSR) system. The influence of the resident time on the particle phase and size was evaluated, and properties of particles derived from systems equipped with differing mixers were compared. The resulting particles were characterized using techniques of X-ray powder diffraction (XRD) analysis, scanning electron microscopy (SEM), and differential scanning calorimetry (DSC). When compared with the Center T-Mixer, results indicate that the Collision Cross-Mixer has better control regarding the morphology and size distribution of resulting particles while improving the transition temperatures of the as-synthesized materials. HWFSR systems containing novel mixer designs are capable of producing pure M-phase VO₂ particles in a single step contrary to the current reactor design that use a second postheat treatment step, and they are capable of synthesizing many other nanoparticle species, especially those requiring high temperature and pressure reaction conditions.

1. Introduction

Thermochromic smart window technologies are attracting tremendous attention due to their ability to regulate infrared heat without noticeable change in visible light transmittance [1]. Vanadium dioxide has shown potential to be utilized as a smart window film material due to its temperature-dependent phase transition behavior in which there are dramatic changes in electrical and optical properties [2]. Among the various existing polymorphs, VO₂ (A), VO₂ (B), VO₂ (M), VO₂ (R) [3], etc., the most suitable polymorph for smart

window applications is VO₂ (M) because of its fully reversible metal insulation transition (MIT) temperature of 68°C, which is significantly lower than the transition temperatures of the other phases [4]. There are several major challenges for current VO₂-based smart window/window films including limitations of the solar transmission modulation (ΔT_{sol}) which is the difference in IR light transmission between the low and high temperature states (usually under 10%), low luminance transmittance (T_{lum}) which is the fraction of visible light transmittance (normally less than 40%), and the high phase transition temperature T_c (about 68°C) [5].

Emerging technologies demonstrate the potential for overcoming these challenges by tuning the particle size, shape, aspect ratio, environment, and doping [6–8].

One of the most convenient routes for VO_2 nanoparticle fabrication is through a hydrothermal reaction [9]. Traditionally, the reaction is performed in an autoclave batch reactor, requiring reaction times of 1–7 days [3] at temperatures and pressures over 220°C and 20 bar, respectively [9], inducing potential explosion hazards. Continuous-flow processing, however, is capable of conducting a hydrothermal reaction more quickly and safely than batch processes with reaction times ranging from a few seconds to few minutes with only a small volume of solution present in the reactor at any one time. In addition, reaction parameters such as temperature, pressure, and resident time are more convenient to control and investigate [10–12] in a continuous-flow process. A two-step route for VO_2 (M) nanoparticle synthesis consisting of a continuous-flow particle production step and a separate postannealing step has been used [13]. However, a postannealing step is not economically efficient for a large-scale production in regard to time and energy consumption. Recently, our group fabricated pure M-phase VO_2 particles using a hot water fluidized suspension reaction (HWFSR) under two minutes [14]. Our novel reaction system uses a traditional T union to mix the hot water solution and reactant which enters through the side. Although the reaction occurring in this system is fast and safe, there is a small deposition of nanoparticles on the metal tubing at the reactor entrance due to a heated stainless steel entrance which initiates particle nucleation early and prior to mixing. In the new HWFSR system, the reactant enters through the bottom of the Center T-Mixer containing a flow distributor and a cooling jacket which prevents the particles from growing on the interior wall of the mixer. This single-step synthesis avoids an additional postannealing treatment step while maintaining the production of pure M-phase VO_2 particles.

Mixing at the entrance is one of the key parameters that trigger instant nucleation and a resulting homogeneous particle size distribution for continuous-flow hydrothermal reaction systems. Unfortunately, a traditional 90° angle T-Mixer is reported to show slower mixing compared with 30° , 50° , and 60° angles or swirling T-Mixers [15, 16]. Other types of passive mixers, including swirling cross mixers [17], micromixers with needle adjustment [18], and center collision mixers [19], are all able to reduce the particle size and increase the uniformity of the particle size distribution but require additional machining and cost.

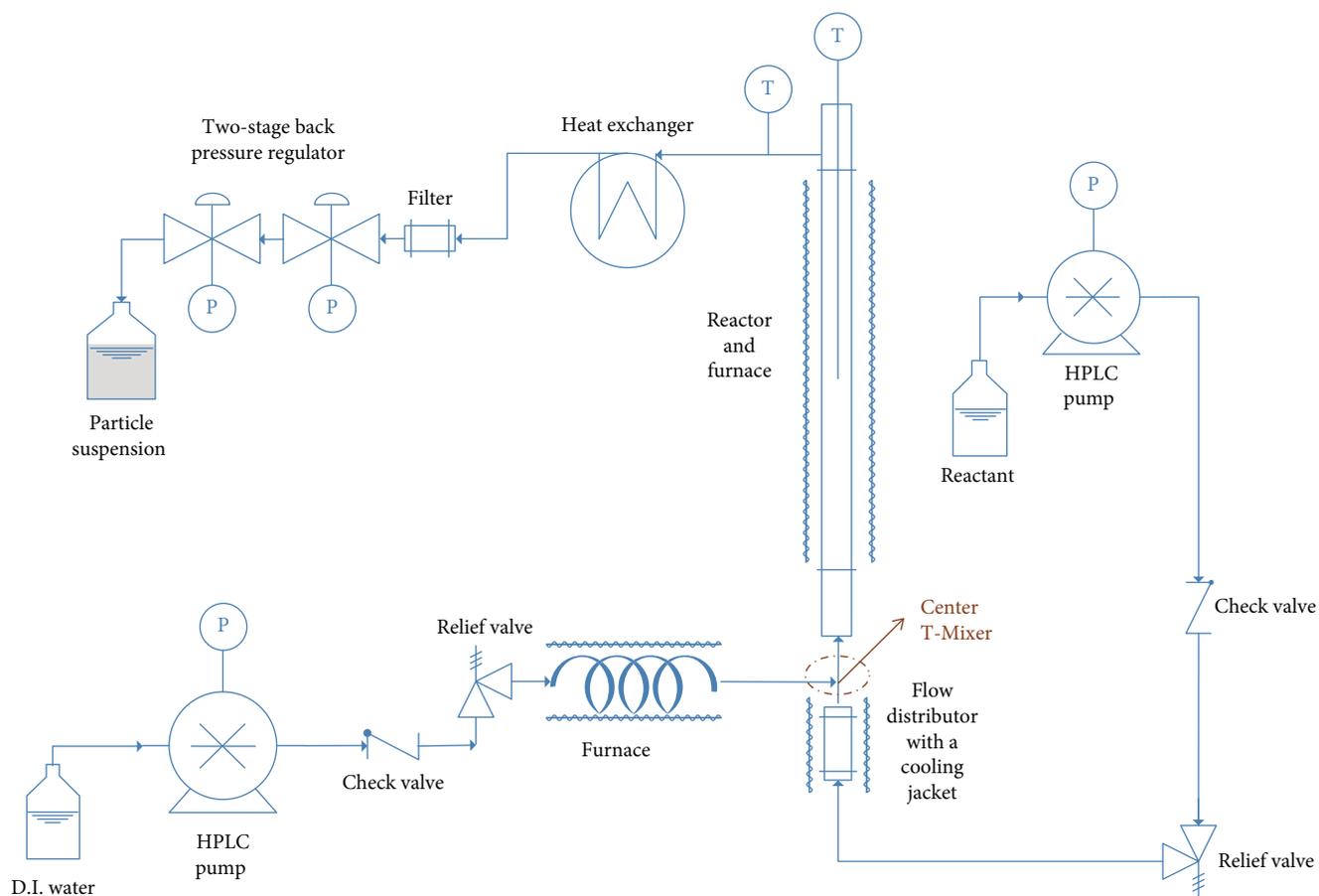
In this research, we continue the development of a hydrothermal continuous-flow process for VO_2 particle synthesis using both a Center T-Mixer and a Collision Cross-Mixer. In the Center T-Mixer, hot water flows out from a small orifice in the center of the T union, before mixing with the reactant solution. The small orifice induces a higher flow rate on the hot water and guarantees a better contact of water with the reactant solution. In the Collision Cross-Mixer, two orifices are used for introducing hot water with a third used for bringing in reactant solution. The collision high flow rate liquid in the center of the cross union creates rapid

mixing of the three groups of flow. VO_2 (M) particles are prepared from the HWFSR system using either a Center T-Mixer or a Collision Cross-Mixer in a single step. Flow rates (resident times) affect VO_2 particle properties. Both mixer styles are compared under various flow rates within the reaction system. When comparing the two styles of mixers, the Collision Cross-Mixer produced smaller VO_2 particles with a narrower particle size distribution. This study also provides a systematic approach and reference for using two differing types of mixers for the hydrothermal continuous fabrication of other nanomaterials.

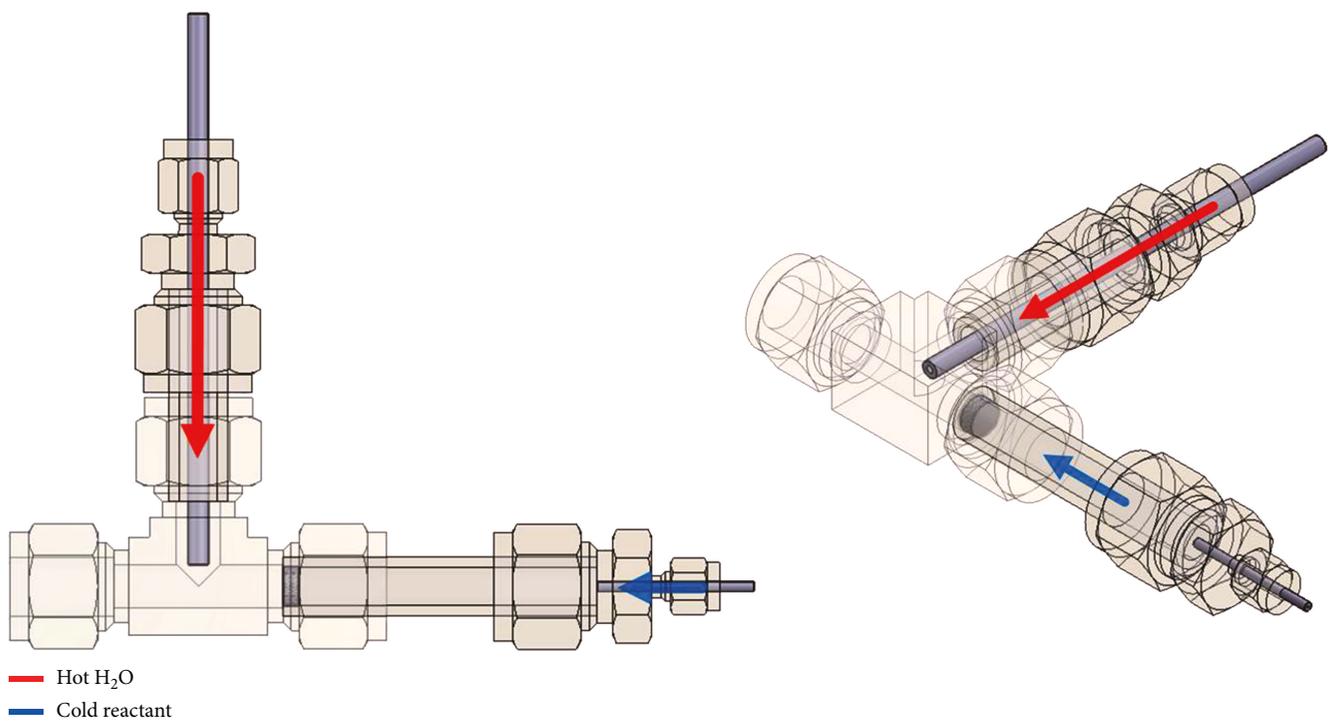
2. Materials and Methods

2.1. Materials, Design of Apparatus, and Procedures. V_2O_5 and $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Sigma-Aldrich) are used as starting materials. In a typical synthesis procedure, an appropriate amount of V_2O_5 and $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (molar ratio 1 : 3) is dissolved in 50 mL, 60 mL, or 70 mL distilled water. The mixture is then left in an ultrasonic bath for 1 hour for thorough mixing and V^{5+} reduction. A dark blue solution is thus formed with a V^{4+} concentration of 0.0712 mol/L. All the chemicals are used without further purification.

The HWFSR system used a Center T-Mixer for this study, as shown in Figure 1(a). A similar setup with a T union instead of a T-Mixer was used by our group previously and is described elsewhere [14]. The current setup contains two HPLC pumps (BlueShadow 40P and BlueShadow 20P, Knauer Inc.): one for the hot water injection stream and the other for the precursor solution. Two check valves (Swagelok Inc.) are used to prevent the gas generated during the reaction from returning to the pumps, and two relief valves (Swagelok Inc.) are used to relieve the system if pressures exceed 250 bar. Prior to the reaction, hot water (10 mL/min, 5 mL/min, or 4 mL/min) is heated up by a furnace (Applied Test System Inc.) to subcritical conditions, and a precursor solution (5 mL/min, 2.5 mL/min, or 2 mL/min) is kept cool by a cooling jacket. Then, the hot water and precursor streams are sent to the mixer system. Mixed in the mixer, the reactant stream is dispersed by an in-house-built distributor containing an inner porous metal substrate (provided by Mott Co.) while the hot water is expelled from a $1/8''$ tube within $3/8''$ T union (Figure 1(b)). Following the mixing, the stream is sent to the tube reactor located within a furnace (Phoenix Flow Reactor™, purchased from Thales-Nano Nanotechnology Inc. to solely use the furnace), which is set to a temperature of 350°C to maintain a reaction temperature of 345°C (which is mainly achieved by the introduction of the hot water stream). In order to cool down the product solution of mostly VO_2 nanoparticles and water after the tube reactor, a heat exchanger (Sentry Equipment & Erectors Inc.) is fixed adjacent to the tube reactor's outlet. Located in series downstream from the heat exchanger, two back pressure regulators (TESCOM, Emerson Electric Manufacturing Co.) maintain a system pressure of 170 bar. An outlet fluid containing VO_2 nanoparticles in the form of a black liquid suspension passes through the back pressure regulators and gets collected by a glass bottle. Then, the suspension is washed seven times using a centrifuge

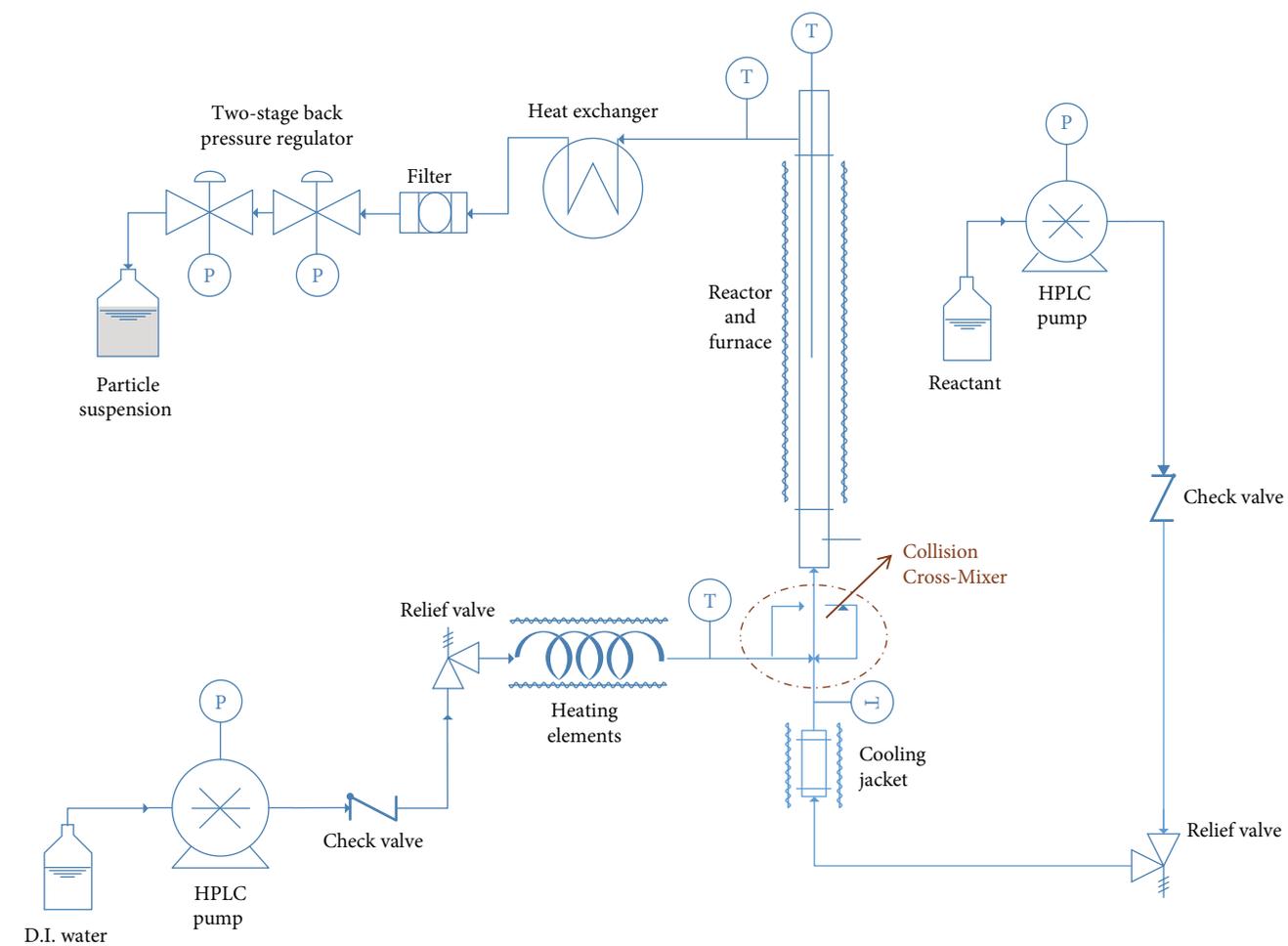


(a)

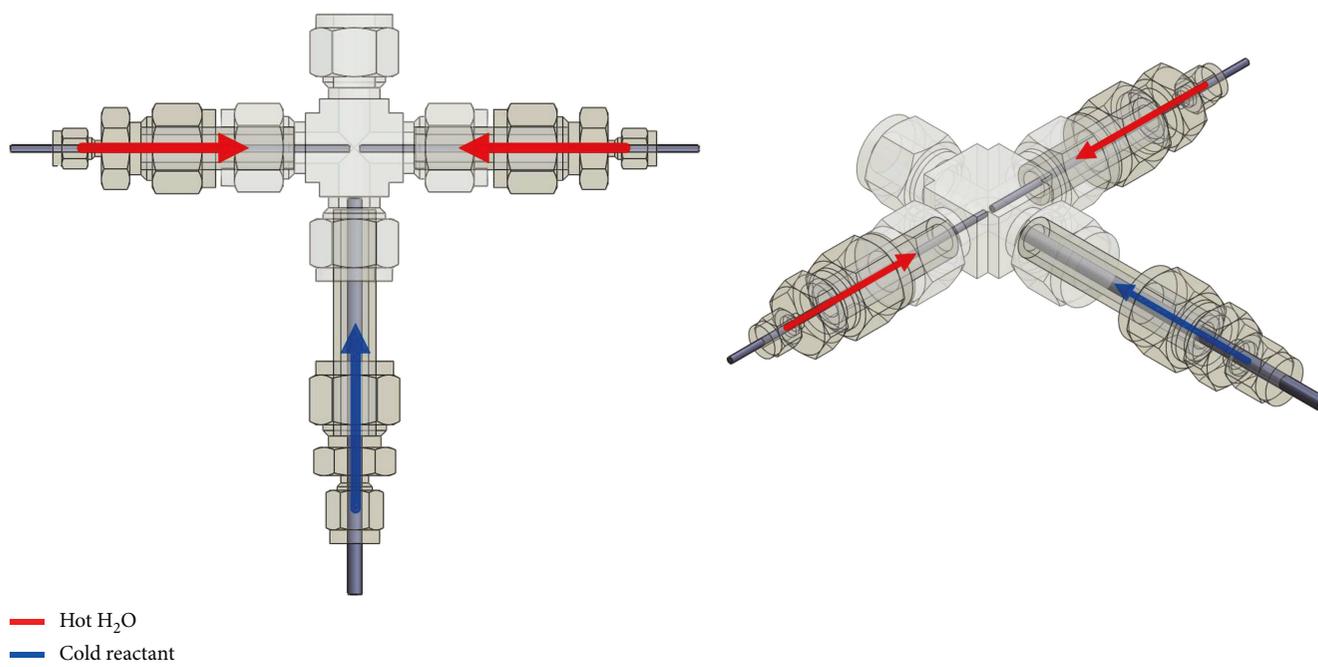


(b)

FIGURE 1: (a) Schematic diagram of the hot water fluidized suspension reaction (HWFSR) system used for VO₂ particle preparation mounted with the Center T-Mixer. (b) A Center T-Mixer.



(a)



(b)

FIGURE 2: (a) Schematic diagram of the HWFSR system used for VO_2 particle preparation mounted with the Collision Cross-Mixer. (b) A Collision Cross-Mixer.

TABLE 1: VO₂ nanoparticle samples prepared via Center T-Mixer and Collision Cross-Mixer mixing systems under various flow rates. (10, 5) represents flow rates of hot water and reactant solution of 10 mL/min and 5 mL/min. All the samples are prepared under reaction temperature of 345°C and a V⁴⁺ concentration of 0.0712 mol/L.

Sample	Mixer type	Flow rate (mL/min)
T1	T	10, 5
T2	T	5, 2.5
T3	T	4, 2
C1	Collision cross	10, 5
C2	Collision cross	5, 2.5
C3	Collision cross	4, 2

(7600 RPM) and ethanol, followed by the collection of the product, a black liquid suspension. Finally, the samples are left in air overnight to dry. All the tubing and fittings for the reaction system were purchased from Swagelok Inc.

Figure 2(a) depicts the HWFSR system using a Collision Cross-Mixer. In this design, the mixer is comprised of a 3/8" cross containing two 1/16" tubes for hot water inlets and a 1/8" tube for a reactant inlet. The hot water enters from both the left and right sides of the cross while the reactant enters from the bottom as shown in Figure 2(b). Every other section of the system is the same as the previously described HWFSR system using a Center T-Mixer Figure 1(a). This new system was designed to enhance mixing between the reactant and hot water, thus leading to more nucleation locations, a more uniform temperature distribution within the reactor, and a more uniform VO₂ nanoparticle size distribution.

2.2. Characterization. The phase purity data is determined by X-ray diffraction (XRD) analysis, which is carried out on a Bruker D2 Phaser using a CuK α 1, a CuK α 2, and a 1% Kbeta line X-ray source and a Lynxeye detector. Scanning was performed over a 2 θ angle ranging from 10° to 70° with a step size of 0.05 units and a rate of 0.1 s/step. The morphology and surface structure of a sample are examined using a scanning electron microscope (SEM) (10 kV acceleration voltage, JEOL 7500) at room temperature. ImageJ software is used to measure the particle diameters. Phase transition properties of the samples are analyzed using differential scanning calorimetry (DSC) (DSC823, Mettler-Toledo International Inc.) with a temperature ranging from 15°C to 90°C, a heating/cooling rate of 2°C/min, and a liquid nitrogen cooling system.

3. Results and Discussion

In this study, six experiments were performed with HWFSR systems, three each using the Center T-Mixer and the Collision Cross-Mixer. Flow rates were 10 mL hot water/min and 5 mL reactant/min (mean residence time: 0.7 min), 5 mL hot water/min and 2.5 mL reactant/min (mean residence time: 1.5 min), and 4 mL hot water/min and 2 mL reactant/min (mean residence time: 1.8 min) as shown in Table 1. These variations in flow rates are used to evaluate the effects

of resident time and the mixer. A reactant temperature of 345°C and a V⁴⁺ concentration of 0.712 mol/L were selected based on former experimental results [14].

Figure 3(a) displays the XRD patterns for samples prepared from a HWFSR system mounted with a Center T-Mixer denoted as T1, T2, and T3. All the samples were shown to be well crystallized, and typical peaks for VO₂ (M), VO₂ (A), and VO₂ (B) phases were detected without phase identification of other possible VO₂ phases. Samples prepared with hot water and reactant flow rates of 10 mL/min and 5 mL/min, respectively, with a mean residence time of 0.7 min produced a mixture of peaks for VO₂ (M), VO₂ (A), and VO₂ (B). As the hot water and reactant flow rates are reduced towards 5 mL/min and 2.5 mL/min, respectively, increasing the mean residence time to 1.5 min, the intensity of XRD peaks for VO₂ (B) phase and VO₂ (A) phase decreases. When the mean residence time is increased further to 1.8 min with corresponding hot water and reactant solution flow rates of 4 mL/min and 2 mL/min, respectively, only peaks corresponding with pure M-phase VO₂ could be identified. The trend indicates that VO₂ (M) particles are more favored with longer resident times. Figure 3(b) shows a similar set of samples fabricated from a HWFSR system mounted with a Collision Cross-Mixer. They exhibit similar phase and crystal indicators as the samples formed from the system mounted with Center T-Mixer.

Morphologies of the particles synthesized from HWFSR systems are displayed in Figure 4. Particles prepared using a Center T-Mixer are shown to have a size distribution ranging from a few nanometers to around 1 μ m in diameter with various rod- and spherical-shaped nanoparticles. When high hot water and reactant solution flow rates of 10 mL/min and 5 mL/min, respectively, were applied, less micron-sized particles were produced, and the portion of large particles became more dominant as the flow rates were lowered (Figure 4(a) T3 and Figure 4(b) T3). As discussed in prior research [14], a longer resident time, while beneficial for producing M-phase particles, results in the aggregation of small particles into larger particles. Additionally, at the entrance of the HWFSR, a differential rate of precursor decomposition and grain growth causes a polarized particle size distribution. Rapid heating and homogeneous nucleation are playing substantial roles in forming smaller and more uniform particles [19]. In this research, the decomposition temperature of the intermediate precursor VOC₂O₄ is 342.9°C [20]. Supersaturation occurs when hot water supplies enough energy to the reactant solution, which then triggers the subsequent nucleation. After the fluid passes the entrance of the mixers, the flow is considered to be laminar with an estimated Reynolds number (Re) between 67 and 168, when total flow rates range from 6 mL/min to 15 mL/min. A nonuniform particle size distribution will trigger differential travelling speeds between larger particles and smaller particles along the reactor, which will increase the probability of particle collision thereby increasing both particle aggregation and elevating the Ostwald ripening. In contrast, if all the particles passing the reactor entrance are of a similar size and shape, the particles tend to not collide with each other under

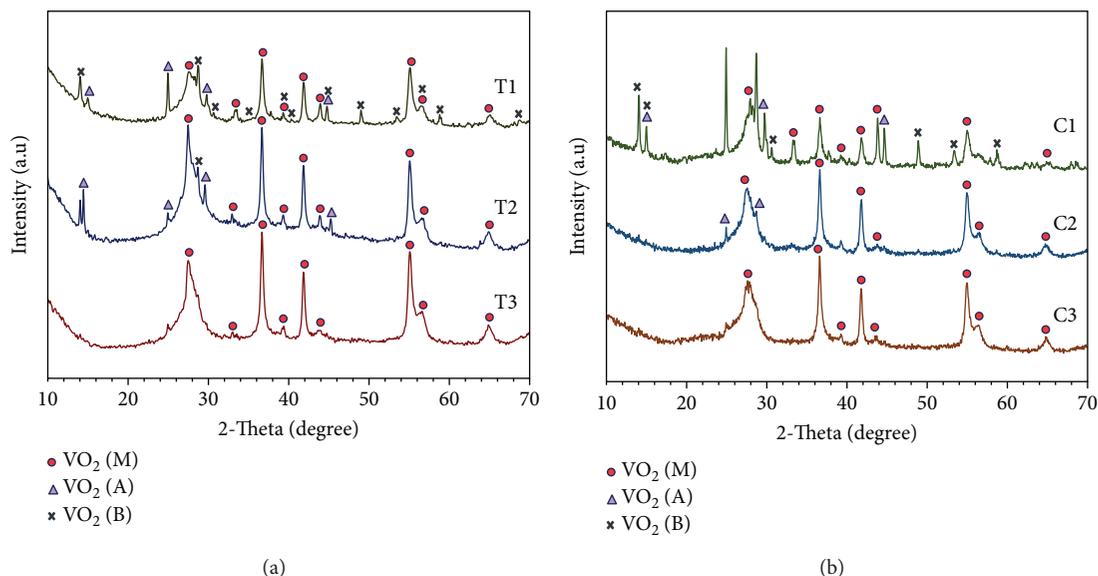


FIGURE 3: The XRD patterns of samples prepared under differing flow rates. (a) Represents samples from a reaction system equipped with the Center T-Mixer, and (b) represents samples from a reaction system equipped with the Collision Cross-Mixer.

moderate concentration and will likely not grow into larger particles before flowing out the reactor. Therefore, choosing the right style of mixer is crucial in regard to both initially and eventually forming monodispersed particles. As observed in Figures 4(a) and 4(b) (C1-C3), the Collision Cross-Mixer (Figure 2(b)) appears to improve mixing when compared to the Center T-Mixer (Figure 1(b)) because it allows entering hot water flow from both sides of the union cross through small orifices rather than only one side. This type of design creates numerous tiny eddies when the two groups of hot fluid from 1/16" tubings meet the reactant solution from a 1/8" tubing. These eddies significantly increase mass and heat transfer between the fluids. Compared with Center T-Mixer, a symmetric mixer design is also beneficial for improving homogeneity of energy dissipation, supersaturation, and the nucleation afterwards. At high hot water and reactant solution flow rates of 10 mL/min and 5 mL/min, respectively, particles formed from the Collision Cross-Mixer mounted system demonstrate better uniformity and sizes up to 400 nm (Figure 4(b)), when comparing them to the nanoparticles formed from the Center T-Mixer mounted system at equivalent flow rates.

When viewing SEM images of samples that were formed utilizing lower flow rates of 4 mL/min and 2 mL/min, the average particle size is larger for both the Collision Cross-Mixer and Center T-Mixer. Longer resident time triggers the aggregation of the particles. However, the undesirable particle growth could be mitigated by applying higher temperature under larger flow rates (shorter resident time) or by utilizing stabilizing agents. In the case of bipolar particle size distribution caused by uneven mixing, longer resident time also assists larger particle growth by consuming smaller particles gradually, which could be explained by the theory of Ostwald ripening. As a matter of fact, microsized VO₂ hollow spheres have been synthesized previously based on this theory in an autoclave reactor [21]. In the same type of

the reactor, the growth of M-phase VO₂ particles was observed by consuming B-phase and A-phase VO₂ particles due to the same reason [3]. In this research, small VO₂ particles are attached on larger ones. The morphologies are identical to microwave-synthesized carbon particles explained by the same Ostwald ripening theory [22]. Nevertheless, due to the fact that only one set of experiments was reported on synthesizing VO₂ via a continuous-flow process prior to this research [13], the direct comparison of Ostwald ripening effect on particle-morphology formation requires more study and is under further investigation by our group. Instantaneous and homogeneous heating alleviates this phenomenon by providing environment for particles to grow uniformly. Particles produced by the Collision Cross-Mixer were much smaller in comparison to those formed using the Center T-Mixer, as well as a narrower particle size distribution (Figures 4(b) and 4(c)). For all of the samples, particles produced using the Collision Cross-Mixer have clear edges in the SEM images, which contrasts the shapeless, blurry particles derived from the Center T-Mixer. A low monomer formation rate versus a high nucleus growth rate may explain this phenomenon. A faster precursor decomposition rate is expected within the Collision Cross-Mixer due to the more efficient instantaneous mixing of hot water and reactant solution compared with the Center T-Mixer. This is in agreement with the fact that particles fabricated under the same reaction conditions (temperature, pressure, residence time, etc.) with different mixers have nonidentical morphologies. A Collision Cross-Mixer can be employed to improve the size, shape, and surface structure of particles while maintaining the requirement of needing pure M-phase VO₂ material.

In order to confirm that the as-prepared M-phase VO₂ particles have thermochromic effects, DSC analysis is conducted as shown in Figure 5. All the samples display MIT temperatures between 29°C and 61°C, which are lower than the reported phase transition temperature of 67-68°C for

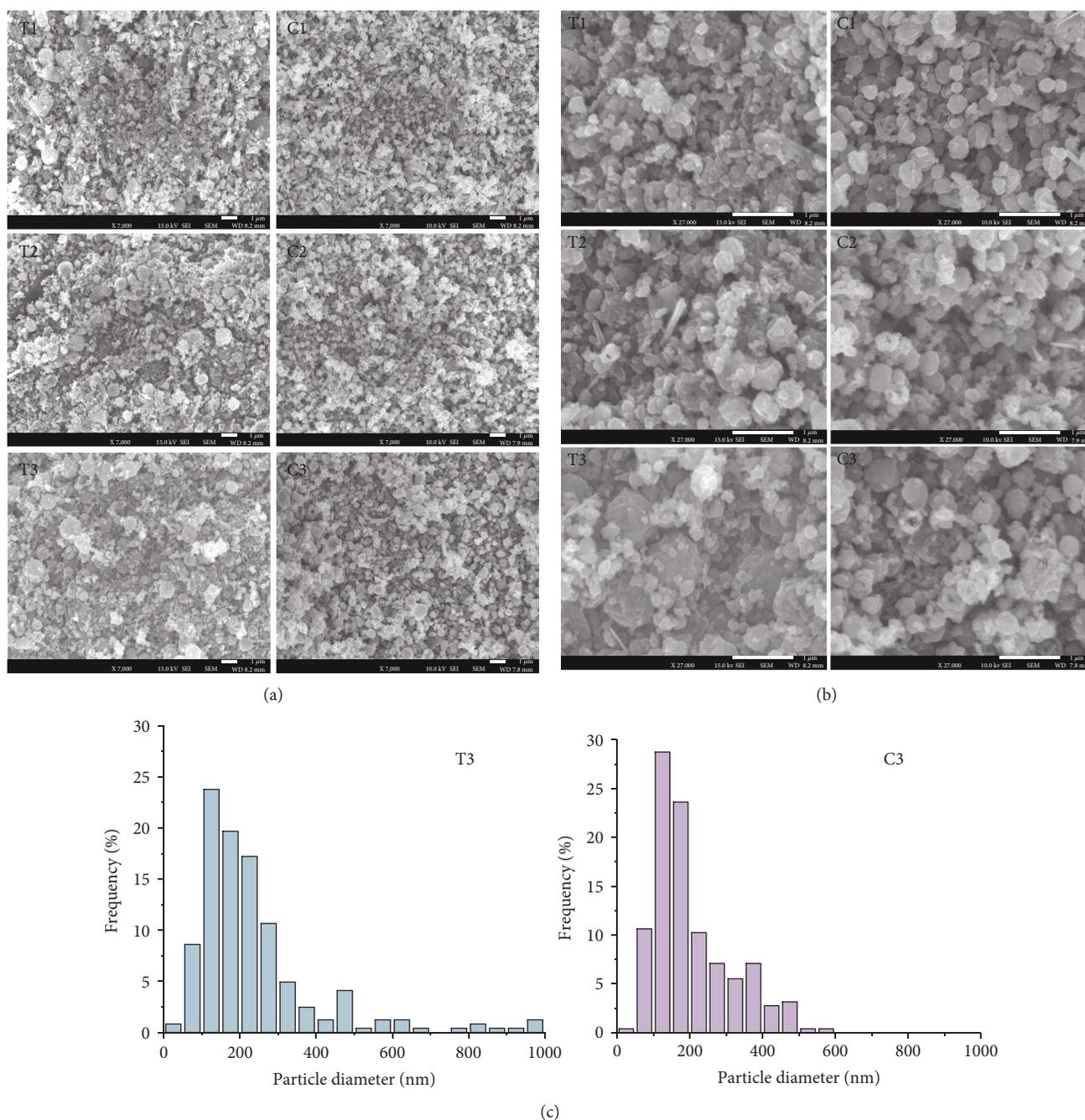


FIGURE 4: (a) The SEM images of samples synthesized under differing flow rates from a system that utilized either a Center T-Mixer or a Collision Cross-Mixer—magnification 7,000. (b) The SEM images of the samples synthesized under differing flow rates from a system that utilized either a Center T-Mixer or a Collision Cross-Mixer—magnification 27,000. (c) Particle size distribution of samples synthesized under flow rates of 4 mL hot water/min and 2 mL reactant solution/min from a system that utilized either a Center T-Mixer or a Collision Cross-Mixer.

bulk VO_2 materials. As discussed in the prior research, many factors could induce a lower MIT temperature, including but not limited to smaller particle sizes [23–25], particle defects, doping [14] (impurities), and film thickness [26]. The reasons are complex, and the transition temperatures of the VO_2 materials differ when applying different synthetic process techniques [27]. The samples synthesized at low hot water and reactant solution flow rates of 4 mL/min and

2 mL/min, respectively, from the Center T-Mixer present MIT temperatures of 54°C when heating ($T_{c\text{-heat}}$) and 39°C upon cooling ($T_{c\text{-cool}}$). Smaller particle size compared with bulk VO_2 might explain the existence of broaden peaks upon heating and cooling from both mixers, which is consistent with the particle size observed from SEM results. However, a narrower peak presents during the cooling process for the material synthesized from the Collision Cross-Mixer.

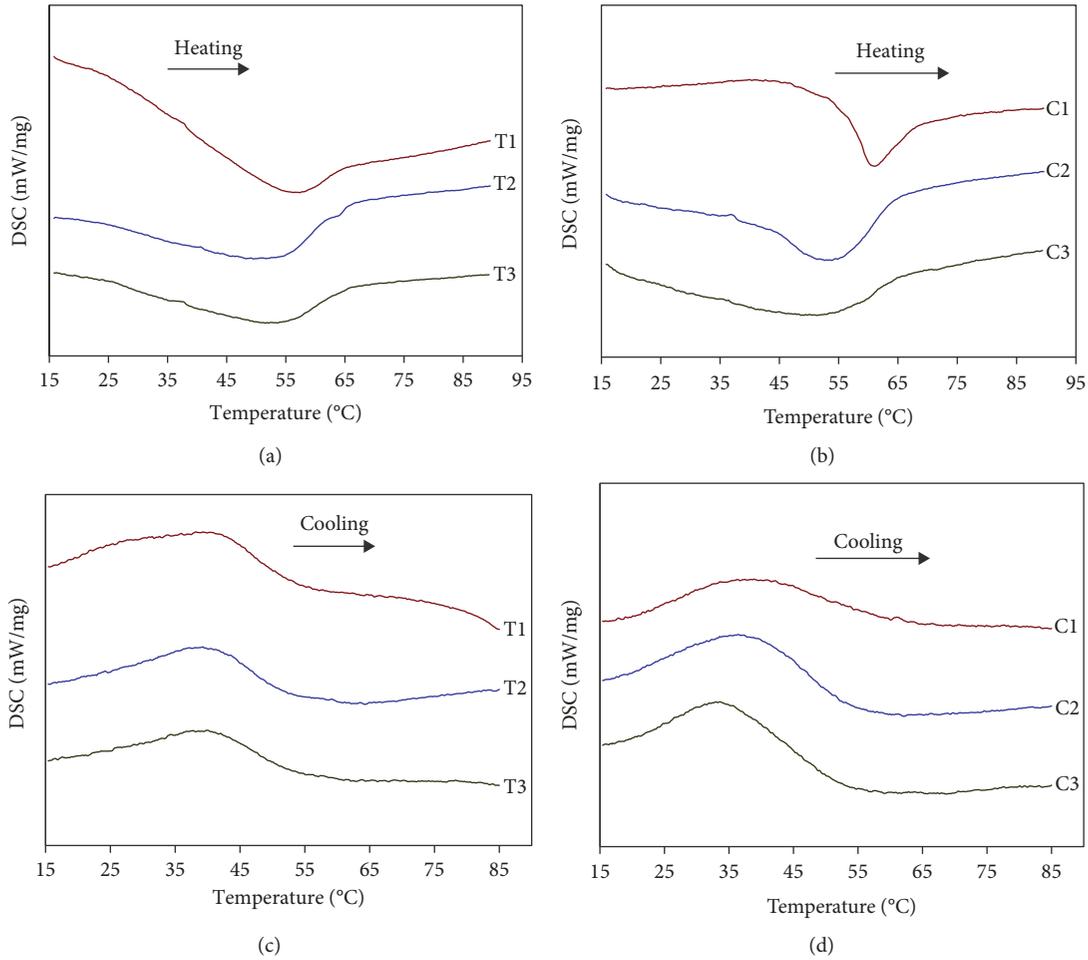


FIGURE 5: The DSC results of VO_2 samples synthesized under differing flow rates from a system that utilized either a Center T-Mixer or a Collision Cross-Mixer: (a, b) heating and (c, d) cooling.

The asymmetric phase transition of VO_2 particles might be explained by the surface defects, which also contributes to the overall change of T_c [1]. Compared with 54°C of $T_{c\text{-heat}}$ from particles produced by using the Center T-Mixer, $T_{c\text{-heat}}$ of particles produced by using the Collision Cross-Mixer has reduced to 51°C . In terms of cooling, $T_{c\text{-cool}}$ has been reduced from 39°C to 34°C by using the Collision Cross-Mixer instead of the Center T-Mixer. This is in agreement with one previous report that smaller particles bring down the $T_{c\text{-heat}}$ temperature [24] but differs from the other reported phenomena on the formation of a $T_{c\text{-heat}}$ temperature higher than 68°C by using smaller VO_2 particles [1, 28]. Despite the complexity of the formation mechanism on an improved $T_{c\text{-heat}}$ and a decreased $T_{c\text{-cool}}$, decreasing T_c from bulk material transition temperature of 68°C without doping is beneficial for VO_2 (M) material synthesis process simplification and process cost reduction for many applications. Additionally, VO_2 particles fabricated by using the Collision Cross-Mixer are more thermally stable compared with those from the Center T-Mixer. DSC analysis (Figure 5) demonstrates a slightly larger latent heat area (Figure 5(d) C3) on particles fabricated from the Collision Cross-Mixer, in contrast to a smaller latent heat area from

particles fabricated under the same condition but with a Center T-Mixer (Figure 5(c) T3). This phenomenon is not significant when dealing with heating curves. Taking into account the potential desired lower switching temperatures from 68°C on VO_2 (M)/ VO_2 (R), DSC results indicate the advantages of producing VO_2 particles by HWFSR mounted with a Collision Cross-Mixer in contrast to that with a Center T-Mixer. It also showcases the potential to decrease T_c by tuning the mixer design and by developing new processes, without introducing extra doping elements. It should be noticed that for samples synthesized with higher flow rates, only a fraction of the VO_2 particles were contributing to the latent heat under 100°C , considering the fact that the MIT of A-phase VO_2 is 162°C [4]. Therefore, samples fabricated with flow rates higher than 4 mL/min and 2 mL/min are purely for reference in this study, indicating that thermochromic effects do exist even for samples with mixed phases.

It is clearly shown that a collision type of the mixing system is capable of improving the morphologies and phase transition temperatures of VO_2 nanoparticles in comparison to the Center T-Mixer, without affecting the phase purity significantly.

4. Conclusions

Continuous-flow hydrothermal syntheses of VO₂ nanoparticles were performed using a hot water fluidized suspension reaction (HWFSR) system mounted with two differing styles of mixers: a Center T-Mixer and a Collision Cross-Mixer. The utilization of a Collision Cross-Mixer resulted in smaller particles with up to 600 nm diameter and a narrower particle size distribution with a shorter mean residence time of 0.7 min when compared to the implementation of a Center T-Mixer that produced a size distribution ranging from a few nanometers to around 1 μm. In addition, pure M-phase particles were obtained from both mixing systems when increasing the mean residence time to 1.8 minutes. Transition temperatures of the as-derived VO₂ particles are also decreased by using the Collision Cross-Mixer. The mixer is cost-effective and convenient for implementation into a microreactor. The reaction procedure is a one-step rapid process without the energy consuming annealing step which is traditionally used to force all A- or B-phase VO₂ particles into pure M-phase material. Furthermore, the safe and fast HWFSR continuous-flow process equipped with designed mixers is applicable for other particle fabrication processes requiring high temperatures and pressures.

Data Availability

The X-ray diffraction analysis and differential scanning calorimetry measurement data on synthesized materials used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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