

Microfluidic Synthesis of Chromium Oxide Microspheres by SOL-GEL Process

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Abstract

A microfluidic platform is developed to synthesize chromium (III) oxide microspheres having a narrow size distribution by sol-gel method. The platform comprises two microfluidic T-junctions, one for mixing of chromium nitrate and HMTA-urea streams and other for segmenting the mixed aqueous phase by an immiscible inert organic phase. A microbore tube follows the second T-junction to provide residence time for the gelation of segmented aqueous phase droplets. Synthesis could be carried out without any choking despite solidification due to gelation in the microbore tube in continuous mode of operation. The effects of the ratio of the flow rates of the organic phase and the aqueous phase on average size and polydispersity index of microspheres are studied. Both parameters are observed to reduce with an increase in flow rate ratio.

Keywords: Microfluidics, T- junction, Sol-gel, Microspheres, Chromium(III) oxide

Introduction

In recent years microfluidic platforms have been explored to synthesize monodispersed microspheres (inorganic as well as polymeric) in continuous mode. This route eliminates the probability of batch to batch variation of the product quality. Moreover, the process can be scaled-up using numbering-up approach. The platform can be used to synthesize microspheres with very narrow size distribution and very good sphericity which are required in many applications. One such application is the synthesis of oxides of nuclear fuel elements like U/Pu/Th for advanced reactors in the form of microspheres^[1]. Typically, the synthesis route for such microspheres involves an internal gelation method (sol-gel) carried out using a gelation column and a dispensing needle (of suitable size) to generate micron sized drops^[2]. However, the size of the setup is relatively larger and throughput of the process is limited by the height of the gelation column.

Microfluidic platforms to synthesize microspheres of nuclear materials have the potential to produce microspheres having narrow size distribution while keeping the setup very compact. Compact setup is of paramount importance while working in constrained environments like fume hood/glove box, which is typically the case for nuclear fuel. Microfluidic platforms can broadly be classified into two categories such as: microchannel-based and capillary-based. Compared to microchannel-based microfluidic platforms, capillary-based microfluidic platforms are easy to assemble and do not need sophisticated microfabrication techniques like photo-lithography etc. Different researchers have used capillary-based microfluidic platforms to demonstrate sol-gel type of reaction. Ye and co-workers used a T-junction followed by a capillary to synthesize CeO_2 microspheres^[3]. Yang and co-workers demonstrated the synthesis of uniform Ce/Eu oxide microspheres with varying Eu

content (7.90%, 13.00%, and 17.56%)^[4]. In the present work, a capillary-based microfluidic platform is used for the synthesis of microspheres of a surrogate material i.e. chromium oxide in continuous mode. The method used in this work is essentially an in-situ technique in which chromium precursor stream and the gelation agent (i.e. Hexamethylenetetramine (HMTA) and urea) are mixed at a T-junction and then the mixed stream is sheared to form monodispersed drops at a second T-junction using a continuous inert organic phase. A microbore tube connected to the second T-junction provides the residence time for gelation to occur in the aqueous phase droplets sheared by the organic phase. The microbore tube is wetted by the organic phase and this prevents choking of the microbore tube even after solidification due to gelation. Since the drop size produced at the second microfluidic junction depends on the flow rates of the mixed aqueous phase and the organic phase, the effect of

organic phase to aqueous phase flow rate ratio (O/A ratio) on the size and polydispersity of the microspheres is studied.

Experimental setup and procedure

Fig. 1 shows the schematic of the experimental setup. Two syringe pumps were used to pump the chromium precursor solution (chromium nitrate) and gelation solution (HTMA-urea) to an 800 μm diameter opposed T-junction, which mixes the two streams. The ratio of molar concentration of HMTA-urea to molar concentration of chromium precursor was maintained at 1.4. A small section of an 800 micron microbore tube was used to transfer the mixed aqueous phase stream to a second opposed T-junction. A third syringe pump was used to pump inert organic phase (dodecane) to the second T-junction. At the second junction, the mixed aqueous phase was dispersed into the continuous organic phase as small drops. This configuration is called as a double T-junction in the rest of this report. The drops generated at the junction thereafter passed through a long microbore tube immersed in a hot bath maintained at 80°C. The drops containing chromium precursor solution as well as HMTA-urea solution formed a gel and got hardened during the residence time provided in the microbore tube. The detailed chemistry of the gelation process is reported elsewhere^[1]. The microspheres coming out of the microbore tube were separated from the organic phase by filtration and then washed thoroughly by CCl_4 to remove traces of organic phase. Thereafter, the washed microspheres were dried to ensure the removal of CCl_4 . This was followed by washing with aqueous ammonia to remove unreacted HMTA, urea and other

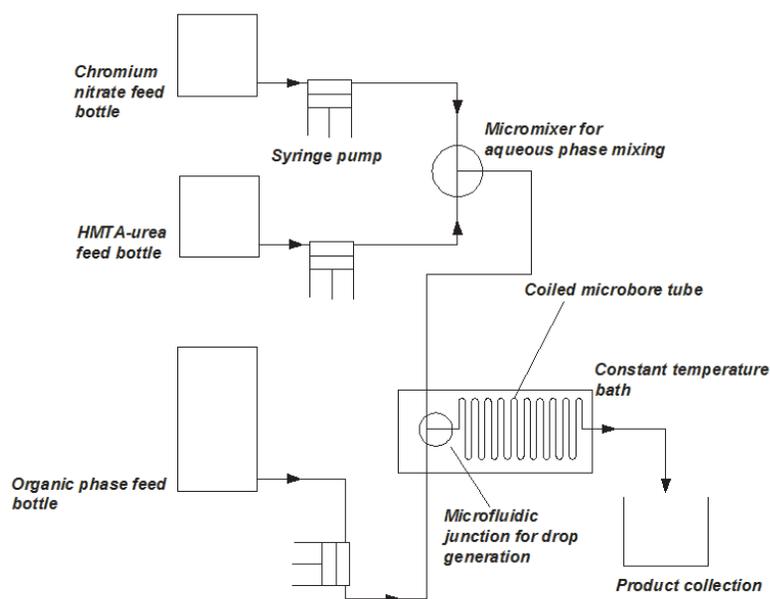


Fig. 1. Schematic diagram of the capillary based microfluidic platform

reaction products. This step was followed by drying at 120°C. The dried samples were observed under an optical microscope. The micrographs were analyzed using ImageJ software and average particle size and polydispersity index were determined. At least 100 particles were measured to arrive at these values. A representative sample was heated to 300°C to remove organic traces and thereafter calcined at 700°C to obtain chromium (III) oxide microspheres. Specific surface area of the sintered oxide microspheres was measured using BET technique and the morphology of the microspheres was observed using SEM.

Results and Discussion

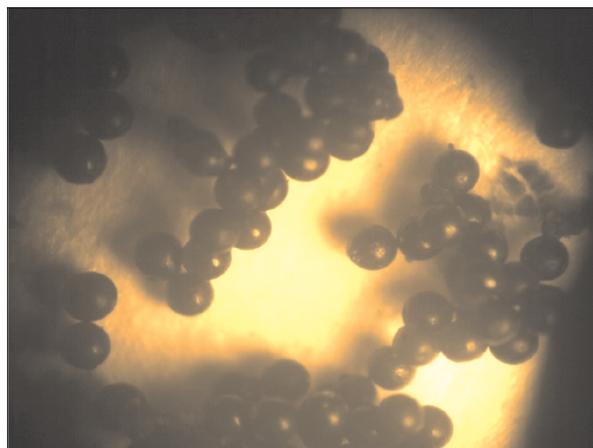
The effect of O/A ratio on average diameter and polydispersity index was studied in detail. Average diameter of the microspheres was estimated by using Eq. (1). Polydispersity index (PDI) is essentially the coefficient of variance

$$d_{10} = \frac{\sum_{i=1}^{i=N} n_i d_i}{\sum_{i=1}^{i=N} n_i} \quad (1)$$

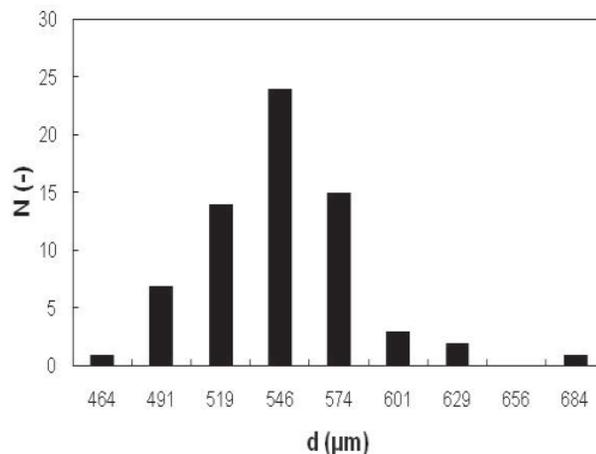
$$PDI = \frac{100 \sqrt{\sum_{i=1}^{i=N} (d_i - d_{10})^2 / (N-1)}}{d_{10}} \quad (2)$$

of the particle size distribution. It was estimated using Eq. (2).

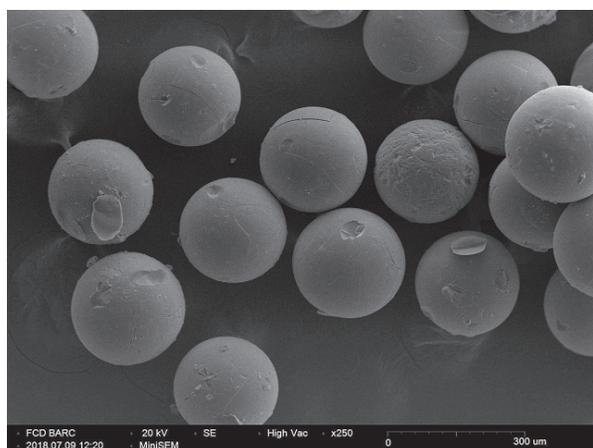
Fig. 2a shows the micrograph of the chromium hydroxide microspheres synthesized at O/A ratio of 60. The diameter distribution is also shown along with the micrograph in **Fig. 2b**. The average diameter is measured to be 579 μm . Polydispersity index is 6.6% which shows that the microspheres are almost monodispersed. The particles were also freely flowing and did not stick to each other after ammonia wash. **Fig. 2c and 2d** show the surface morphology of the calcined microspheres observed by SEM. The microspheres are found to be spherical with a smooth surface. The specific surface area of the microspheres as obtained from BET analysis is found to be 30 m^2/gm . The room temperature XRD pattern of Cr_2O_3 microspheres calcined at 700°C for 2 h was recorded. It is shown in **Fig. 3**. The pattern observed matches well with the Cr_2O_3 PDF# 38-1479.



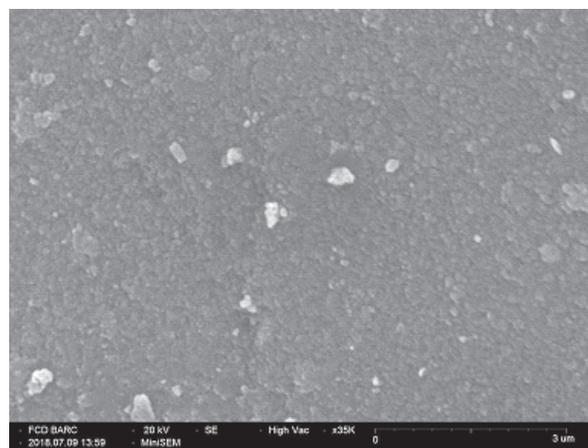
(a)



(b)



(c)



(d)

Fig. 2. (a) Micrograph of chromium hydroxide microspheres (b) size distribution of the chromium hydroxide microspheres and (c) & (d) morphology of the sintered chromium oxide microspheres by SEM at two magnifications

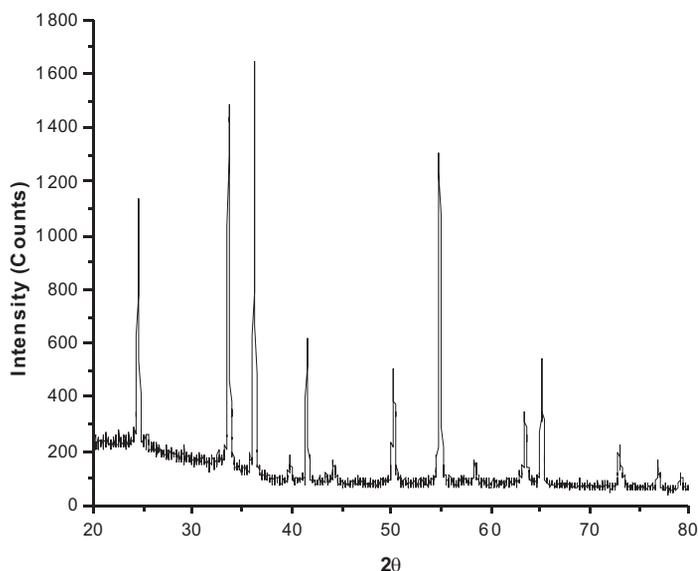


Fig. 3. Room Temperature XRD pattern of Cr₂O₃ microspheres calcined at 700°C for 2 h

Repeatability of the experiments was also checked. The variation in average size of microspheres for identical flow conditions was very less (< 4%). The effect of O/A ratio on average diameter and polydispersity index was also checked. **Fig. 4** shows the effect of O/A ratio on average diameter and polydispersity index. Flow rate of mixed aqueous phase was 0.05 mL/min. It can be observed from **Fig. 4** that an increase in O/A from 30 to 60 reduced the diameter of microspheres by as much as 28% (i.e. from 788 to 579 μm). Also the polydispersity index is observed to reduce from 10.5% to 6.6%. For the same flow rate of the aqueous phase, higher flow rate of the organic phase inflicts more shear force on the

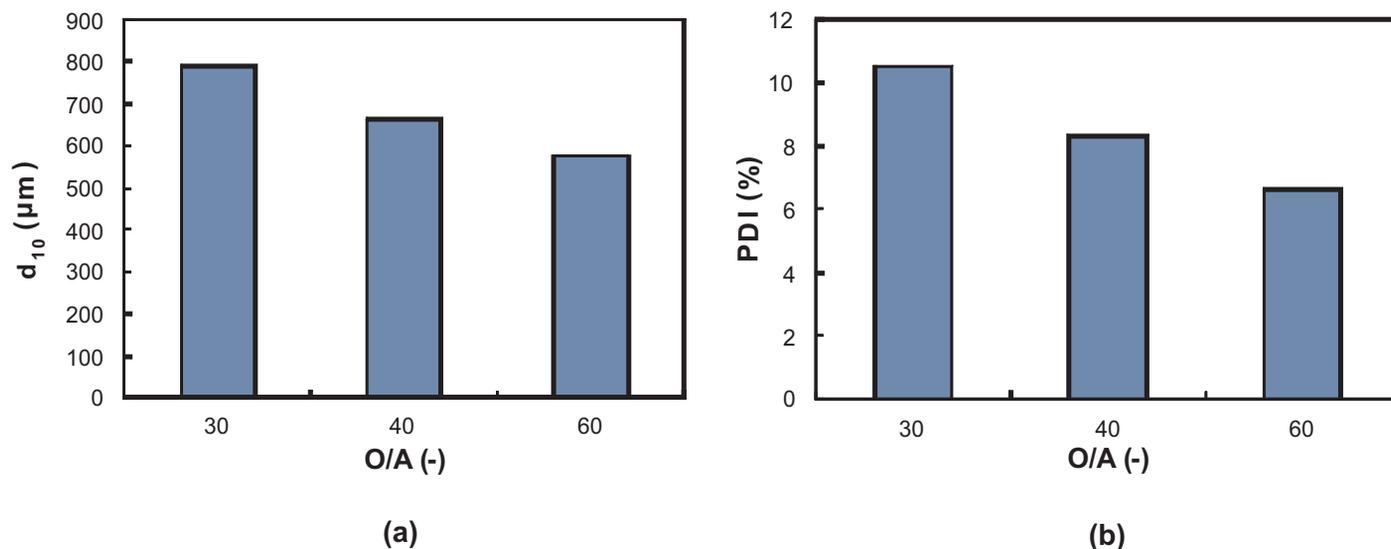


Fig. 4. Effect of O/A ratio on (a) average particle size and (b) polydispersity index

liquid-liquid interface at the microfluidic junction. This leads to faster drop breakage resulting in smaller drops of the aqueous phase. Furthermore, at high O/A ratio disturbances that may lead to formation of drops of different diameters are damped significantly thus reducing the polydispersity index. Hence, it can be concluded that formation of smaller microspheres with narrower size distribution is favoured at high O/A ratio. This also shows that it is possible to obtain microspheres of desired size range by varying the O/A ratio.

Conclusion

A capillary microfluidic platform is developed for the synthesis of chromium oxide microspheres in continuous mode with a narrow size distribution through sol-gel route. It comprises a double T-junction configuration and a 800 μm diameter microbore as the microreactor. The first microfluidic junction is used to mix chromium precursor (i.e. chromium nitrate) and HMTA-urea streams. The second microfluidic junction is used to disperse the mixed aqueous stream in the form of small droplets using an immiscible inert organic phase. Chromium oxide

microspheres obtained from the microfluidic route were free flowing, spherical and had smooth surface. Average diameter and polydispersity index were observed to reduce with increase in the flow rate ratio of the organic phase and the mixed aqueous phase (O/A ratio) which makes it possible to obtain microspheres of desired size by varying the operating conditions. For O/A = 60, spherical particles of 579 μm average diameter and 6.6% polydispersity index were obtained. The work reported in this study is with chromium nitrate as a surrogate. The platform can be modified and optimum conditions can be identified to synthesize microspheres of nuclear fuel elements.

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