MICROFLUIDIC SYNTHESIS OF METAL ORGANIC FRAMEWORKS CRYSTALS INTO CONFINED MICRODROPLETS

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ABSTRACT

A microfluidic strategy has been used to e continuously synthesized and study a well known Metal Organic Frameworks such as Cu_3BTC_2 into microdroplets. High quality crystals were obtained within a few minutes with reaction kinetics increased by approximately two orders of magnitude compared to the conventional batch processes. The effect of the flow rate and the concentration on the crystallinity and BET surface area were also studied.

KEYWORDS

Cu_3BTC_2, Metal Organic Frameworks, droplet, microreactor

INTRODUCTION

Metal-organic frameworks (MOFs) are a new class of porous crystalline materials composed by metal connectors and organic ligands that have attracted immense attention due to the possibility to obtain a large variety of diverse structural topologies, pore sizes and volume and chemical functionalities.[1] The design of MOFs with tunable properties has opened therefore perspectives for these materials utilization in many fields such as in gas storage, gas separation, catalysis, sensing and biomedical applications. [2] The conventional synthesis of MOFs is usually carried out via hydrothermal or solvothermal methods and requires several days for the crystallization and formation of the highly porous network. [3] However, the development of continuous, rapid and viable processes is required in order to meet commercial and industrial requirements.

The utilization of droplet-based microfluidic has been extensively exploited for high screening biological and biochemical experiments for the last decades. The microfluidic approach for material synthesis offers several advantages such as the very efficient mixing into confined droplets that leads to increased reaction’s rate and the possibility to track in-situ the material formation by optical microscopy. [4,5] In addition the use of microdroplets rather than continuous flow permits to avoid a critical issue such as the channel clogging, in presence of solid particles. In this work, we report a microfluidic strategy to perform the continuous and ultra-fast synthesis of Metal Organic Frameworks crystals into confined microdroplets. In particular synthesis of the material Cu_3BTC_2 is described and the influence of the flow rates as well as the precursor concentration have been investigated

EXPERIMENT

The material Cu_3BTC_2 is reported as case of study; the conventional solvothermal synthesis of this MOF is performed at 90°C for 24 hours [6]. The Cu_3BTC_2 precursor solution was prepared by adding a stoichiometric amount of $Cu(NO_3)_2{\cdot}H_2O$ and H_3BTC to a homogeneous solution of *N,N*-dimethylformamide (DMF), Ethanol (EtOH) and deionized water (H_2O). The schematic illustration of the microsystem is shown in Figure 1 (a).

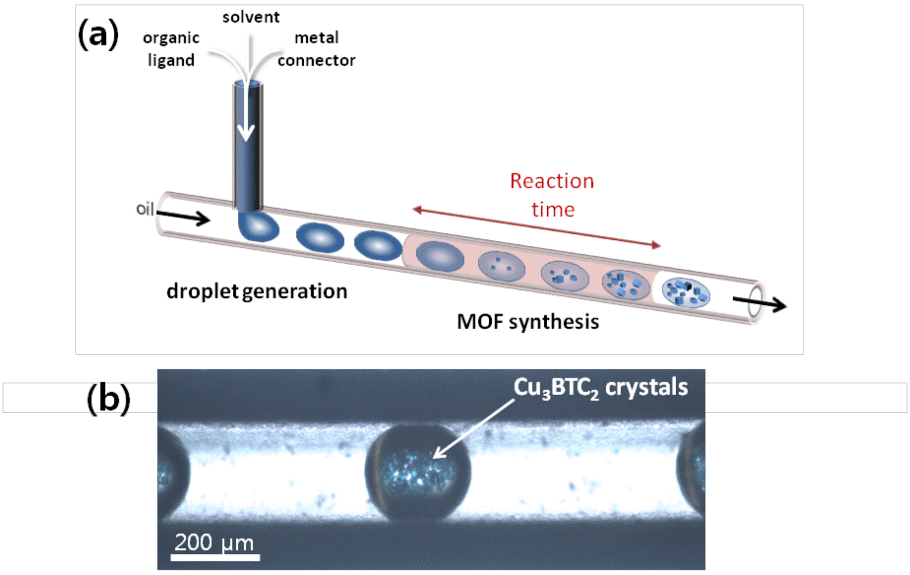

Figure 1: (a) Schematic representation of the microfluidic system; (b) optical image of one single droplet containing Cu_3BTC_2 crystals

The microdroplets containing the Cu and BTC precursors are first generated in a PDMS based T-junction device prepared by scaffold method.[7] The structure of the PDMS chip allows easy and direct connection between the droplet generation device and the PFA tube without leaking or droplets merging. In the second step, the droplets passed through the PFA tube immerse in a silicon oil bath at 90°C in order to perform the solvothermal synthesis of MOF crystals into the droplets. The optical image in Figure 1(b) show discrete 200µm droplets containing the characteristic bluish Cu_3BTC_2 crystals formed after reaction. After reaction, the synthesized products were collected at the outlet of the PFA tube by a cooled vial at low temperature to avoid further crystallization. Then, the upper oil phase (continuous phase) was separated, and the synthesized products were collected by centrifuging (4000 rpm, 15 minutes). After washing several times the as-obtained samples with fresh EtOH, the resultant products were dried at 80 °C overnight under vacuum.

The experiments were carried out at various flow rates of dispersed phase (Qd; 1-12 $\mu L\ min^{-1}$) and continuous phases (Qc; 5-60 $\mu L\ min^{-1}$) with constant ratio Qd:Qc = 1:5. The reaction time, which corresponds to the retention time of the droplets in the heating bath, was fixed between 1 and 12 minutes by controlling the flow rates of both oil and polar phases. This parameter has been modulates in order to investigate the influence of the retention/reaction time on the morphology, the crystallinity and the inner porosity of the crystals obtained from the precursor solution having initial copper concentration equal to 0,6 mol/L. The morphology of the resulted crystals is shown in SEM micrograph in Figure 2: the particles consist of the typical octahedral Cu_3BTC_2 crystals in the 5-15 µm range.

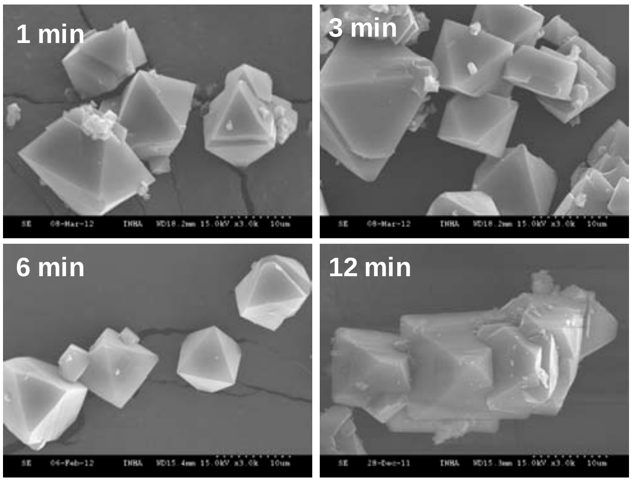

Figure 2. (a) SEM micrograph of the obtained Cu_3BTC_2 crystals for increasing reaction times

The X-ray diffraction patterns of the resulted crystals obtained after increasing retention times are shown in Figure 3(a): the characteristic peaks corresponding to the crystalline structure of Cu_3BTC_2 can be identified for all the samples even after one minute of reactions. The most important properties to evaluate the quality of the material are its specific surface area (S_{BET}) and its pore volume. Those values have been calculated by BET ads that are reported in Figure 3(b) for all the retention times.

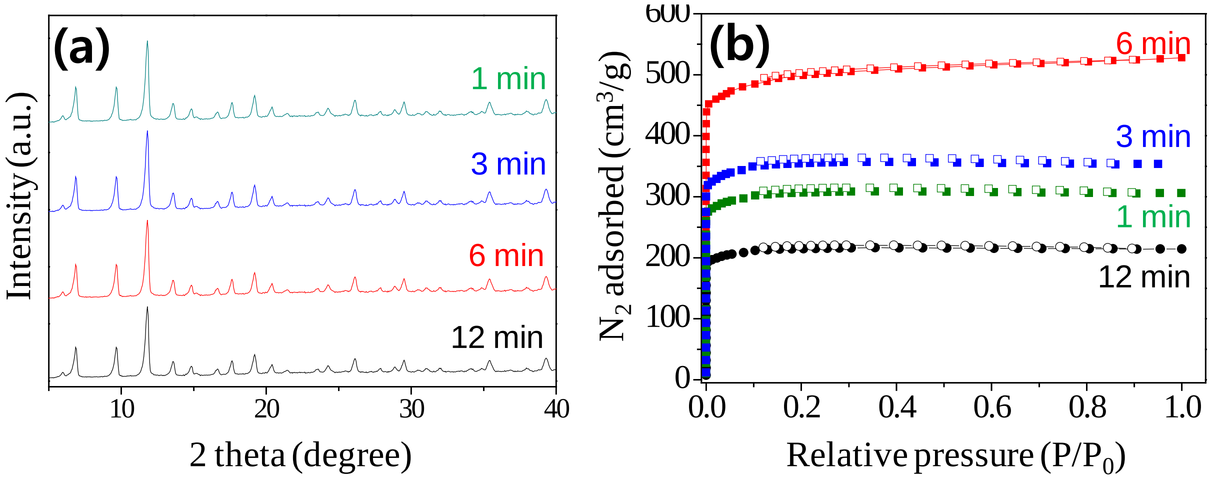

Figure 3. (a) XRD patterns and (b) BET curves of the Cu_3BTC_2 crystals obtained after increased retention time

The effect of the retention time on S_{BET} is summarized in the graph in Figure 4 for two different precursor solution concentrations: 0,12 and 0,6 M as referred to the copper content. In both cases a similar trend was found with an optimum reaction time that gives a maximum S_{BET}. In particular high quality crystals can be obtained after only 3 minutes of reaction from the lower concentrated precursor solution: S_{BET} surface was found to be 1913 m^3/g, a higher value compared to the conventional bulk process performed for 24 hours. In addition a decrease of S_{BET} at higher retention times indicates a fast degradation of the crystals due to the metastable nature of the material and its redissolution in the mother solution especially in the presence of H_2O; Cu_3BTC_2 is known to be moisture-sensitive [8]

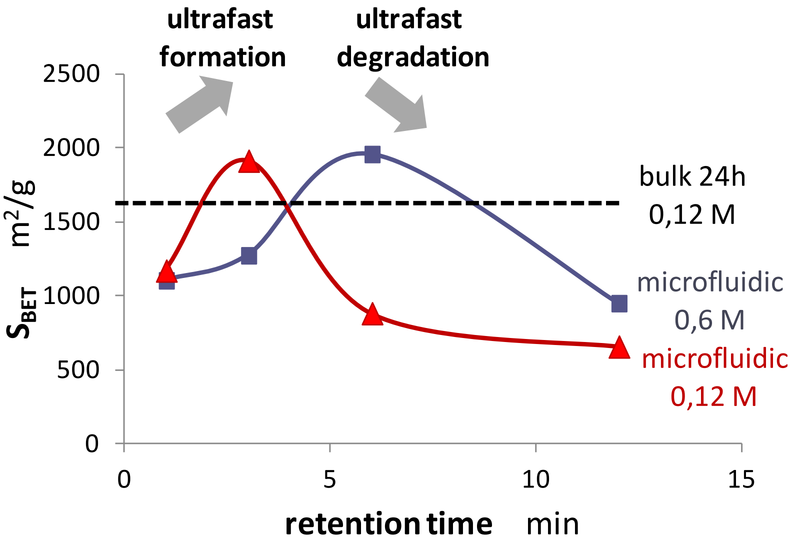

Figure 5. Specific surface area as function of the retention time and of the concentration.

In summary a new microfluidic strategy was developed in order to synthesize Metal Organic Frameworks into microdroplets in a continuous and fast way. In particular the preparation of Cu_3BTC_2 crystals was performed within few minutes with increased crystallization (and degradation) kinetics: this process can be thus considered as an ideal platform for the development and the continuous production of novel MOFs.

REFERENCES

[1] O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H. K.Chae, M. Eddaoudi, J. Kim, *Nature*, 2003, 423, 705-710.
[2] M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka, S. Kitagawa, *Angew. Chem., Int. Ed.Engl.* 1997, 36, 1725-1730.
[3] N. Stock, S. Biswas, Chemical Reviews, **112**, 933 (2012).
[4] S.S. Chui, S.M.O Lo, I.D. Williams, *Science*, 1999, 282, 1148-1151.
[5] P.H. Hoang, C.T. Nguyen, J. Perumal, D.P. Kim, *Lab Chip* 2011, 11, 329.
[6] P.H. Hoang, H.S. Park, D.P. Kim, *J. Am. Chem. Soc.* 2011, 133, 37, 14765.
[7] A. Asthana, K. O. Kim, J. Perumal, D. M. Kim, D. P. Kim *Lab Chip*, 2009, 9, 1138.
[8] J. B. Decoste, G.W. Peterson, M.W. Smith, C.A. Stone, C. R. Willis, *J. Am. Chem. Soc.* 2012, 134, 1486.

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