

液滴式微流控芯片制备沸石咪唑骨架材料

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摘要 沸石咪唑骨架材料(zeolitic imidazolate frameworks, ZIFs)因其大比表面积、规则孔道结构、骨架可调控、水热稳定性等特点, 在吸附、分离和催化领域具有广阔的应用前景. 本工作基于模板法设计和制备双“T”型连续液滴式微流控芯片, 通过多相持续进料, 稳定快速合成单斜晶C2/c ZIF-7(方钠石结构), ZIF-8和Co-ZIF-8等材料, 从而减少产物的差异性. 微流控芯片连续制备得到的ZIFs具有非常高的结晶度和均一性. 此外, 通过调节起始反应物浓度和停留时间, 实现了ZIFs产物粒径和形貌的调控. 微流控芯片提供了一种简易可控快速宏量制备ZIFs材料的新方法.

关键词 沸石咪唑骨架材料, 液滴式微流控芯片, 连续合成, 过程强化, 宏量制备

金属有机骨架材料(metal organic frameworks, MOFs)是一类由过渡金属离子与有机配体通过配位键形成具有规则多孔结构的新型纳米材料^[1,2]. Huang等人^[3,4]使用Zn²⁺与咪唑衍生物配位合成了具有SOD拓扑结构MOFs, 首次制备了具有代表意义的开放孔金属多氮唑框架材料(metal azolate frameworks, MAFs)^[5]. 在此基础上, 研究人员以Zn²⁺, Co²⁺等金属离子为阳离子, 咪唑或类咪唑类有机物为配体, 系统地合成了大量二价金属多氮唑材料, 并深入研究了其结构和性能^[4,6-8]. 这类材料形成的金属-有机配体-金属键角与传统沸石分子筛中Si-O-Si键角相似(145°), 因此也称这类材料沸石咪唑骨架结构材料(zeolitic imidazolate frameworks, ZIFs). ZIFs材料具有比表面积大、孔道结构规则等特征. 对于不同的咪唑衍生物, 因其分子大小及官能团的差异, 引起ZIFs材料孔结构和骨架性质的变化, 从而实现材料的性能

调控. 此外, ZIFs材料具有良好的化学稳定性和水热稳定性, 因此在吸附、分离、催化和限域合成等方面均表现出了广阔的应用前景^[6,9].

ZIFs主要通过无溶剂法、溶剂热法、液相扩散法等合成, 通过变换金属离子和咪唑配体制备具有不同拓扑结构的纳米多孔材料^[6,10]. 溶剂是影响ZIFs性能和产率的重要因素. 甲醇作为最常用的溶剂, 有助于制备均匀ZIFs晶体材料, 但是甲醇溶剂中反应速率和反应物产率都较低, 严重限制了ZIFs材料的快速制备^[11,12]. Zhu等人^[13]首次提出氨水和甲醇混合溶剂可显著提高ZIFs材料的产率, 研究发现氨不仅有助于咪唑配体的去质子化, 而且作为配位缓冲液有助于提高金属离子与配体间的配位速率, 从而提高反应产率. 目前ZIFs的制备方法主要采用间歇式的制备方法. 但是间歇式的合成方法过程耗时长、收率低, 且容易导致不同批次产物性能差异, 在规模化制

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备时容易引起放大效应。虽然微波辅助、超声辅助、微乳液合成等方法也用来强化ZIFs材料的合成过程,但是受到设备和操作过程的影响,合成过程效率低下。因此,采用连续式制备方法,强化合成反应过程,是实现均一ZIFs材料宏量制备理想方法。

微流控技术是一类在微米尺度空间内对微流体精准操控的技术。微流控芯片因其高比表面积、强传热传质效率、安全性高和放大效应小等特点,成为强化反应过程、宏量制备和安全生产中常用的技术,在过程强化反应器制备、精细化学品合成和纳米材料制备等领域广泛应用^[14-17]。本文针对ZIFs材料传统间歇式合成过程中耗时、收率低等问题,采用多相连续式液滴微流控芯片合成多种ZIFs。实验采用甲醇氨水混合溶剂,在微通道内强化合成过程中的混合传质效率,快速制备ZIFs材料。考察浓度和反应时间对产物的影响,优化反应条件,实现ZIFs材料的宏量制备。

1 实验

(i) 材料和设备。聚二甲基硅氧烷(polydimethylsiloxane, PDMS)母液和交联剂(Daw Corning Co.); 矿物油(黏度: 23.90~27.01 cSt(1 cSt=10⁻⁶ m²/s, 40℃), BEANTOWN Chemical); 硝酸锌(AR, >99%, 北京化工试剂厂); 硝酸钴(AR, >99%, 天津市福晨化学试剂厂); 2-甲基咪唑(Mim, AR, >98%), 苯并咪唑(Bim, AR, >98.5%, 天津希恩思生化科技有限公司); 司盘80 (SPAN 80, TCI, 上海); 甲醇(AR, >99.5%, 北京市通广精细化工); 氨水(AR, 25%~28%, 北京市通广精细化工)。

微量注射泵(6槽, 申辰泵业有限公司); 聚四氟乙烯管(PFA tube, 外径(OD)=1.5 mm, 内径(ID)=0.5 mm, 上海恒佳实业有限公司); 不锈钢毛细管(OD=

0.5和0.81 mm, 银龙不锈钢有限公司)。

(ii) 微流控芯片的制备和ZIFs的合成。双“T”型液滴式微流控芯片的制备参照文献[18]中的模板制备法并略做改动。如图1所示, 将不锈钢毛细管(OD=0.81 mm, L=80 mm)两端与PFA管相连, 然后将另外两段不锈钢毛细管(OD=0.5 mm, L=100 mm)用胶水垂直粘在水平不锈钢管上构成微通道模板。随后用双面胶将构建的微通道模板支撑在塑料培养皿底部。将PDMS母液与交联剂按10:1比例充分混合、脱气, 随后将脱气PDMS前驱体小心倒入培养皿至淹没微通道模板3~5 mm。将培养皿静置10 min后放入70℃烘箱中固化2 h。用刀片把固化后的PDMS从培养皿中取出, 然后将PDMS中通道模板小心地取出, 再用丙酮、乙醇充分洗涤PDMS芯片通道除去可能的残留物。将清洗后的PDMS芯片置入80℃烘箱中进一步固化2 h, 最终制备得到双“T”型微流控芯片。

如图2所示, 用PFA管将微量注射泵与PDMS芯片各进料口连接, 其中反应物A和B分别从垂直进料口进料, 连续相C从水平口进料。另外将1 m长(V=196.26 μL)PFA管与PDMS芯片连接作为反应管, 通过不同注射泵分别控制反应物A、B和连续相C的流量(Q_A , Q_B 和 Q_C), 进而控制反应物在反应管中的停留时间。当停留时间为1 min时, $Q_A=Q_B=50$ μL/min, $Q_C=96$ μL/min; 当停留时间为5 min时, $Q_A=Q_B=10$ μL/min, $Q_C=20$ μL/min。将一定量Zn²⁺或Co²⁺金属离子溶于甲醇和氨水(1:1, v:v)中, 作为溶液A; 将Mim或Bim溶于相同溶剂中作为溶液B, 并保持金属离子与配体的摩尔比为1:3; 矿物油(1%(质量百分比) SPAN 80)作为连续相C。连续相通过剪切力将反应物溶液剪切为液滴。原料在PFA中反应一定时间后, 用离心机在9500 r/min转速下离心分离10 min收集产物, 产物依次用石油醚、甲醇洗涤3次。最后将产物置于

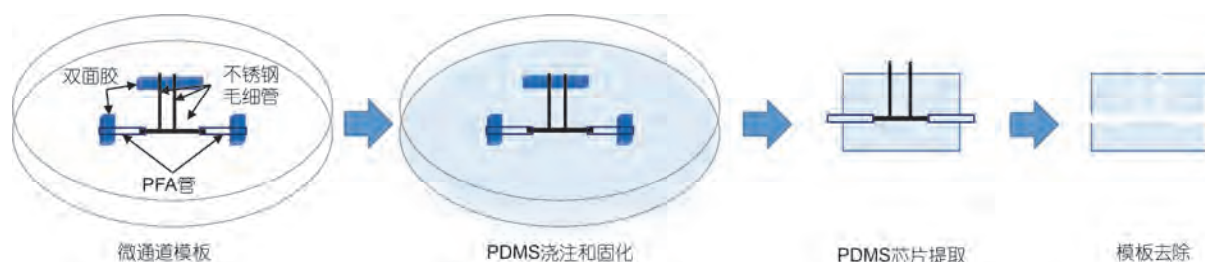


图1 (网络版彩色)模板法制备双“T”型液滴式微流控芯片步骤

Figure 1 (Color online) The fabrication procedure of dual “T” droplet microfluidic chip

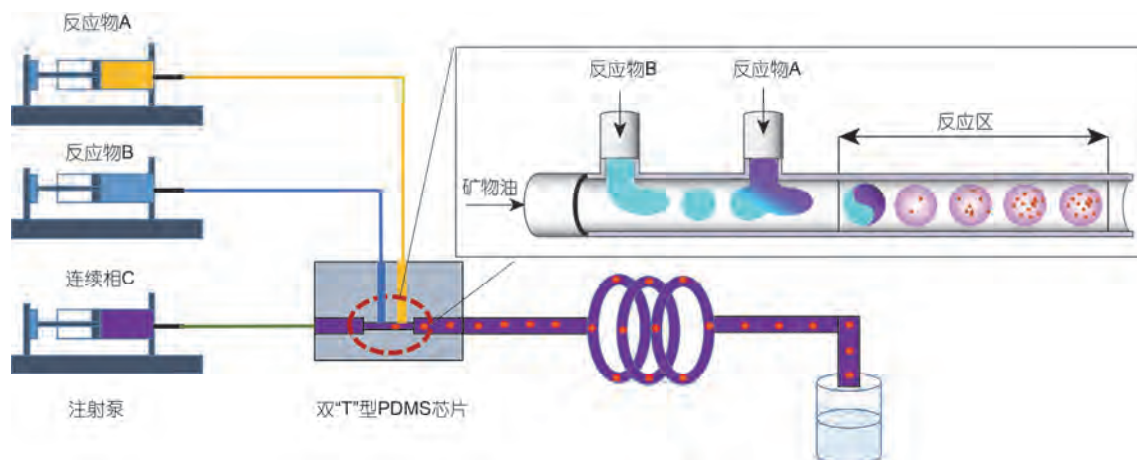


图2 (网络版彩色)微反应系统合成ZIFs示意图

Figure 2 (Color online) Illustration of the synthesis of ZIFs in microfluidic system

70℃真空干燥箱中干燥24 h用于测试。

(iii) 样品表征. 采用扫描电子显微镜(SEM, HITACHI S-4700, 日本)表征ZIFs材料微观表面形貌; 样品的物相和结构分析由X射线衍射仪XRD, (2500VB2型, 日本理学株式会社)测试并记录; X射线光电子能谱仪(XPS, ESCALAB 250Xi, 美国赛默飞世尔科技公司)用来对ZIFs材料结构进行分析。

2 结果与讨论

2.1 微流控芯片

图3(a)是通过模板法制备的双“T”型微流控芯片。透明PDMS芯片完整复制了模板结构形成“T”型通道(图3(b))。经过后热固化处理, PFA管可以与微流控芯片紧密地连接在一起, 并能承受一定的压力, 在总流量 $Q=400\ \mu\text{L}/\text{min}$ 等情况下稳定运行无泄漏。这是因为弹性PDMS材料在热处理过程中产生了轻微的收缩。轻微的形变既不影响PFA与微流控芯片的连接, 又提高了微流控芯片的密封性能。图3(c)是Co-ZIF-8合成过程中液滴融合图片, Mim溶液在第1个“T”型通道口被矿物油剪切为液滴, 然后与第2个“T”型通道金属离子溶液融合(图2), 融合后液滴快速流入PFA反应管进行混合反应。

2.2 产物分析与表征

表1归纳本工作中制备ZIFs的条件以及相应产率和时空产率。ZIF-7(也熟知为MAF-3), ZIF-8(也熟知为MAF-4)和ZIF-67作为被广泛研究的ZIFs^[5,6], 是本

微流控合成中主要研究的材料。产物收率(Y)基于反应物Zn的量按式(1)计算, 相应时空产率(STY)按式(2)计算:

$$Y = \frac{\text{目标产物质量}}{\text{理论目标产物质量}} \times 100\%, \quad (1)$$

$$\text{STY} = \frac{\text{产物质量}}{\text{反应体积} \times \text{时间}}. \quad (2)$$

从表1中可以看出, 在甲醇和氨水混合溶剂中, 除合成ZIF-67反应外, 其他反应在停留时间为1 min时, 都得到了相应的固体颗粒产物, 说明在微流控过程强化下, 可以实现ZIFs的快速合成。本工作同时利用单“T”通道进行合成, 但是由于合成速率较快, 大量固体产物堆积在“T”型通道口, 随着系统运行时间的增加堵塞微通道, 从而使得微反应器不能长时间稳定运行。因此, 一些研究人员通过增加反应管直径、提高流速、降低反应物浓度、降低反应速率等方法来降低通道堵塞问题^[13,19,20]。本工作中采用液滴融合的方式进行合成, 由于反应发生在液滴中, 有效地避免固体产物堆积, 从而使得微反应器可长时间稳定运行。通过计算可得 ZIF-7具有最高的收率, 而ZIF-67在反应条件下基本无固体产物生成, 收率为0。多个研究已证明氨水及有机碱在 Zn^{2+} 与2-甲基咪唑等配体配位过程中具有去质子化、活化金属离子能力和中和反应中生成的硝酸等作用, 是ZIFs材料合成速率提高的重要因素^[11,19,21], 而本实验结果说明混合溶剂对 Co^{2+} 离子与2-甲基咪唑配位的促进作用较小。通过调节反应物浓度, 研究其对产物的影响。由表1结果可知, 增加反应物进料浓度, 不仅提高了ZIFs产

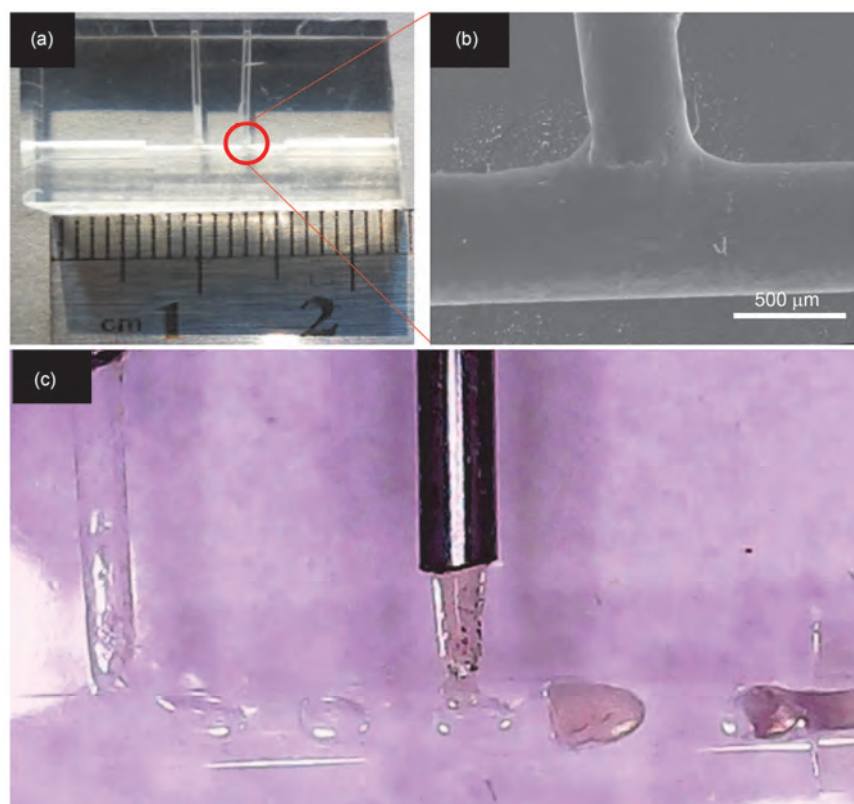


图3 (网络版彩色)微流控芯片的表征. (a) PDMS微流控芯片; (b) “T”型通道的SEM图片; (c) Co-ZIF-8在双“T”型微流控芯片中的合成

Figure 3 (Color online) Characterization of microfluidic chips. (a) The optical image of PDMS chip; (b) the SEM image of “T” shape channel; (c) the synthesis of Co-ZIF-8 in dual “T” droplet microfluidic chip

表1 ZIFs材料合成条件

Table 1 The synthesis condition for different ZIFs

样品序号	反应物A	反应物B	停留时间(min)	收率(%)	时空产率(kg/(m ³ d))
ZIF-7(单斜C2/c), Zn ₄ (Bim) ₁₆	Zn(NO ₃) ₂	Bim			
1			1	56	214
2	50 mmol/L	150 mmol/L	5	60	46
3			1	60	461
4	100 mmol/L	300 mmol/L	5	64	100
ZIF-8 Zn(Mim) ₂	Zn(NO ₃) ₂	Mim			
5			1	42	68
6	50 mmol/L	150 mmol/L	5	45	15
7			1	81	267
8	100 mmol/L	300 mmol/L	5	83	55
ZIF-67 Co(Mim) ₂	Co(NO ₃) ₂	Mim			
9			1	0	—
10	50 mmol/L	150 mmol/L	5	0	—
11			1	0	—
12	100 mmol/L	300 mmol/L	5	0	—
Co-ZIF-8 M(Mim) ₂	Zn(NO ₃) ₂ +Co(NO ₃) ₂	Mim			
13			1	17	29
14	25 mmol/L (Zn)+25 mmol/L (Co)	150 mmol/L	5	32	11
15			1	48	160
16	50 mmol/L (Zn)+50 mmol/L (Co)	300 mmol/L	5	52	34

物的收率,而且显著地提高了产物的时空产率.然而,在反应管长度固定的情况下,增加反应时间,虽然产物收率有一定提高,但是导致反应器时空产率急剧缩小,不利于产物的宏量制备.因此在收率变化不大情况下,缩短反应时间可有效提高时空产率.

产物的物相纯度和结构通过XRD谱图表征.图4(a)是在混合溶剂中合成的ZIF-7材料XRD谱图.不同条件下合成的ZIF-7材料都具有较窄的特征峰,说明产物具有较好的结晶度.同时这些特征峰与文献[22,23]中单斜 $C2/c$ ZIF-7晶相(方纳石结构, $Zn_4(Bim)_6$)的典型特征峰一致,说明本实验条件下所有产物均为均一的致密晶相.单斜晶 $C2/c$ ZIF-7(方纳石结构)由Yang等人^[24]于2008年首次发现,是一种具有平面正方形网状结构固体.许多研究工作已经证明,在含水的氛围下,具有多孔性的菱方 $R\bar{3}$ 和三斜 $P\bar{1}$ ZIF-7晶相会逐渐转化为密实的单斜 $C2/c$ ZIF-7晶相^[22,25].本实验中,混合溶剂虽然提高了

ZIF-7的合成速率,但是由于氨水的存在,导致生成的产物以致密结构为主.单斜 $C2/c$ ZIF-7相是ZIF-7结构中最致密的一种结构,也是其较为稳定的原因之一. ZIF-8和Co-ZIF-8样品的XRD谱图具有清晰的尖峰,这些峰位置与ZIF-8材料的方纳石结构模拟计算峰位置完全一致,且没有任何其他峰出现,证明在微流控芯片中合成了均一的方纳石结构产物(图4(b)).由于Zn和Co所形成的晶体结构一致,我们对Co-ZIF-8样品进一步进行了表征.图4(c)是ZIFs的光学照片,单斜 $C2/c$ ZIF-7晶相和ZIF-8为白色固体粉末,而Co-ZIF-8样品显示淡紫色,证明产物中含有Co元素.此外,对Co-ZIF-8进行了XPS分析以验证Co存在和配位环境.如图4(d)所示,Co 2p峰的出现说明Co-ZIF-8中含有Co.对Co 2p进行分峰处理可得3个主要的峰.其中电子结合能为782.0 eV的峰归属于饱和配位的Co-N₄, 780.5 eV的峰为晶体结构中不饱和配位的Co-N_x ($x < 4$),而786.3 eV的峰主要为固体外

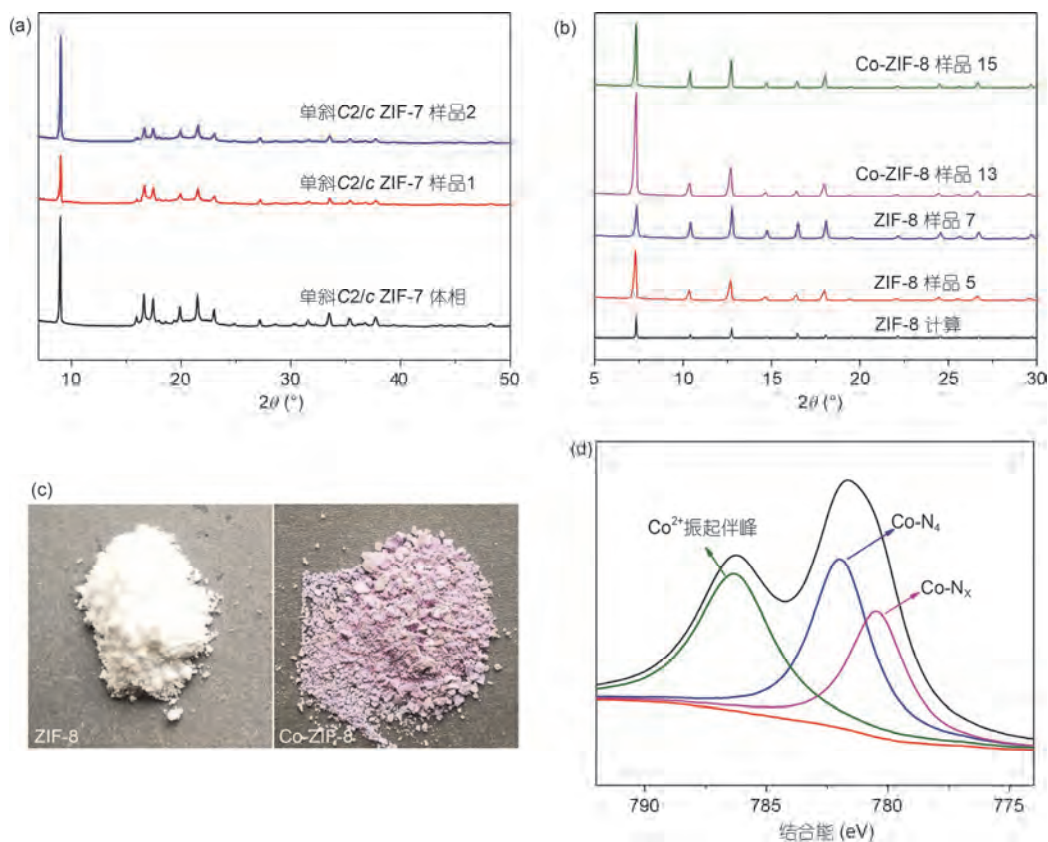


图4 不同样品的XRD谱图. (a) 单斜 $C2/c$ ZIF-7 材料; (b) ZIF-8 和Co-ZIF-8 材料; (c) ZIF-8 和Co-ZIF-8 光学照片; (d) Co-ZIF-8 的Co 2p XPS拟合曲线

Figure 4 (Color online) The XRD patterns of monoclinic $C2/c$ ZIF-7 (a), ZIF-8 and Co-ZIF-8 (b), optical images of ZIF-8 and Co-ZIF-8 (c), Co 2p fitting peak of Co-ZIF-8 (d)

表面或缺陷处的少量 Co^{2+} 的振起伴峰^[26-28]。XPS结果说明Co离子通过配位键掺杂在Co-ZIF-8的结构中。

图5是不同浓度和不同反应时间得到单斜C2/c ZIF-7的SEM图片。从图中可以看出,所有单斜C2/c ZIF-7样品呈现不规则颗粒的形貌,部分颗粒具有球形形貌。说明混合溶剂条件下,单斜C2/c ZIF-7较快的反应速率导致固体各向生长速率相似,进而生成不规则球形颗粒。样品3和4比样品1和2固体颗粒大,说明随着反应物浓度的提高,固体颗粒的粒径也随之增大。当反应时间从1 min增加至5 min时,相同反应物浓度下,产物颗粒也增大(样品2>样品1,样品4>样品3),说明随着反应时间增加,固体颗粒逐渐变大。如表1中单斜C2/c ZIF-7计算所得收率,随着浓度和反应时间的增加,单斜C2/c ZIF-7的收率增加,与固体颗粒粒径的变化一致。

图6是不同浓度和不同反应时间得到ZIF-8的SEM图片。ZIF-8的合成与单斜C2/c ZIF-7的规律相似。随着反应物浓度提高及反应时间的增加,反应收率提高,同时纳米颗粒的大小也略微增加。与单斜C2/c ZIF-7不同的是,反应1 min时,ZIF-8颗粒更加均匀,并呈现出多面体结构,包括六面体、八面体等多种结构。随着反应时间增加至5 min,ZIF-8逐渐生长为以六面体颗粒为主,夹杂部分十二面体的固体产物。这是因为氨水对配体去质子化促进反应平衡向ZIF-8生长的方向移动,导致晶体向各方向生长,得到均匀生长六面体晶体颗粒^[29,30]。同时由于反应速

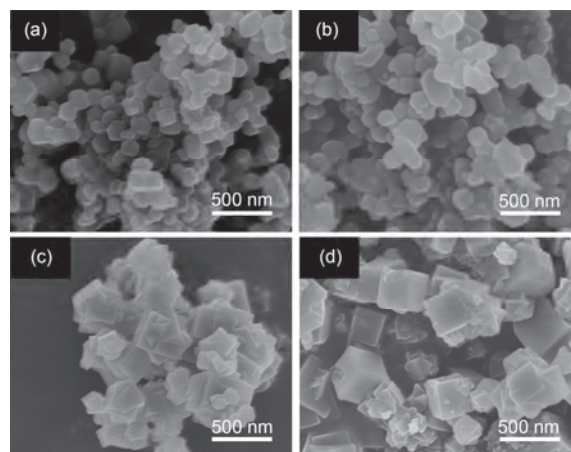


图6 不同条件下合成ZIF-8的SEM图片。(a) 样品5;(b) 样品6;(c) 样品7;(d) 样品8

Figure 6 The SEM images of different ZIF-8. (a) Sample 5; (b) sample 6; (c) sample 7; (d) sample 8

率较快,ZIF-8的颗粒相互堆积在一起,部分颗粒甚至相互嵌在一起。

ZIF-67在本实验的合成条件下几乎没有固体颗粒的生成。说明该合成条件对ZIF-67的形成没有促进作用。因为ZIF-8可以在此条件下快速合成,同时研究人员发现Co掺杂ZIF-8具有优异的光学和电化学性质^[31,32]。因此,本工作采用混合金属源,制备Co-ZIF-8。图7是不同浓度和不同反应时间得到Co-ZIF-8的SEM图片。尽管样品13和样品15固体颗粒都为十八面体,都包含有6个{100}表面和12个{110}表面,但这两个样品形貌依然有较大区别。低

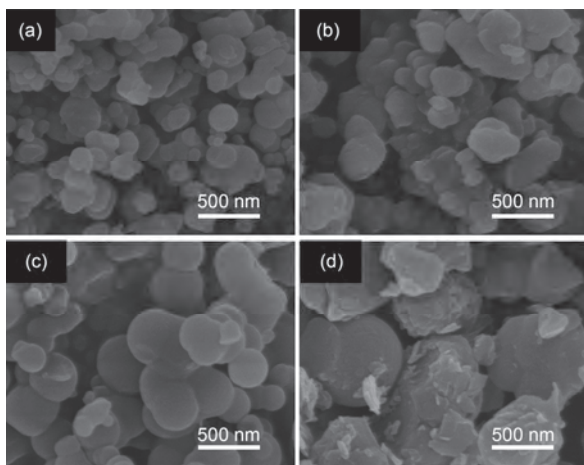


图5 不同合成条件下单斜C2/c ZIF-7的SEM图。(a) 样品1;(b) 样品2;(c) 样品3;(d) 样品4

Figure 5 The SEM images of different monoclinic C2/c ZIF-7. (a) Sample 1; (b) sample 2; (c) sample 3; (d) sample 4

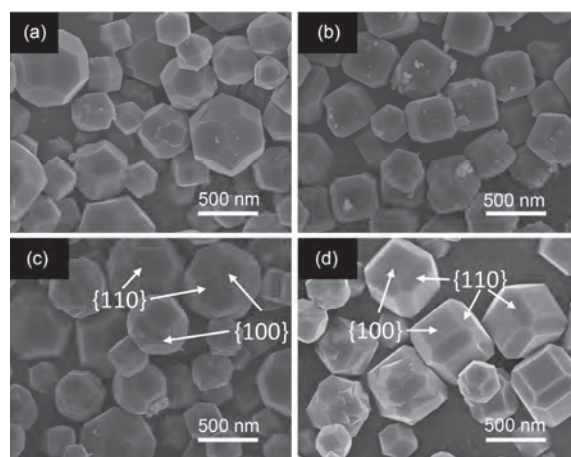


图7 不同条件下合成Co-ZIF-8的SEM图片。(a) 样品13;(b) 样品14;(c) 样品15;(d) 样品16

Figure 7 The SEM images of different Co-ZIF-8. (a) Sample 13; (b) sample 14; (c) sample 15; (d) sample 16

反应物浓度的样品13的{110}晶面范围很大,以至于固体颗粒形成了类似球体的十八面体颗粒,而高浓度样品15的{100}晶面范围较大,得到类似正方体的十八面体结构,这说明Co的掺杂量影响了ZIF-8的形貌.其原因可能是因为 Co^{2+} 在混合溶剂中形成ZIFs结构的速率较慢,因此随着Zn浓度的提高,掺杂样品更接近于ZIF-8的形貌.从图6(c)和(d)可以看出,反应时间对产物形貌影响较小,但是产物粒径有一定增大,这与另外几种ZIFs合成类似,随着反应时间的增加,产物颗粒逐渐长大.

3 结论

本实验通过设计和制备双“T”型液滴式微流控芯

片,在室温下连续快速制备具有不同形貌的ZIFs材料.微流控芯片液滴内的动态合成过程极大地提高了原料间的混合扩散效率,强化了ZIFs合成的微观过程,实现单微流控芯片中单斜C2/c ZIF-7($461 \text{ kg}/(\text{cm}^3 \text{ d})$), ZIF-8($267 \text{ kg}/(\text{cm}^3 \text{ d})$)和Co-ZIF-8($160 \text{ kg}/(\text{cm}^3 \text{ d})$)的宏量制备.此外,微流控芯片连续式合成过程显著地降低了间歇式制备导致的产物差异性,最终得到均一致密结构的单斜C2/c ZIF-7和均一方钠石结构的ZIF-8及Co-ZIF-8,且所有产物都具有非常高的结晶度.通过调节原料浓度和反应时间不仅可实现产物收率和时空产率的调控,还能实现对产物颗粒大小和形貌的调控.因此,微流控芯片提供了一种简单易控的快速宏量制备ZIF材料新方法.

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Summary for “液滴式微流控芯片制备沸石咪唑骨架材料”

Synthesis of zeolitic imidazolate frameworks in droplet microfluidic system

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The zeolitic imidazolate frameworks (ZIFs) have been extensively investigated in adsorption, separation and catalysis for their unique properties, e.g., high surface area, ordered pore structures, tailorable frameworks and high chemical and thermal stability. Zn^{2+} and Co^{2+} are mostly used metal cations in ZIFs synthesis, because they prefer to form tetrahedron structures with imidazoles and their derived organic ligands. However the conventional preparation methods, which are generally performed at solvothermal condition in the sealed vessel, are time consuming and inhomogeneous process at micro-scale. As a result, the products are always different from batch to batch, which limits the scale-up of ZIFs by conventional synthesis methods. Therefore, facile ways to avoid these problems occurred in ZIFs synthesis are still needed to develop. The microfluidic system is of great advantages such as high surface to volume ratio, high mass and heat transfer efficiency and continuous flow processing. The continuous droplet microfluidic system is effective in mixing for the dynamic micro-environment inside droplets, and it is also effective in reducing the clogging problems for the confined synthesis of nanoparticles inside the microdroplets. Hence the droplet microfluidic system has been widely applied in nanomaterials synthesis. In this work, we design and fabricate a dual “T” type droplet microreactor to overcome the disadvantages of batch synthesis. The PDMS microchip was fabricated by a scaffold template assisting thermal curing process. Various ZIFs, including monoclinic *C2/c* ZIF-7, ZIF-8 and Co doped ZIF-8, were first synthesized in this microfluidic system to demonstrate a universal applicable synthesis method. The concentration of starting material and reaction time were studied in the synthesis of all ZIFs in this work. The results indicated that the increasing of concentration and retention time led to the increasing particles' size in all ZIFs, as well as the increasing of product yield. However, the space-time yield was dramatically decreased while the retention time increased from 1 to 5 min, while the yield was just slightly increased. It was because that the micro-synthesis process had been significantly intensified in 1 min for the high mixing and diffusion efficiency in the microfluidic system. Moreover, the mixture solvent of methanol and ammonia water strongly facilitated the formation of ZIFs as well. The high throughput microfluidic system showed an estimated space-time yield of monoclinic *C2/c* ZIF-7 (461 kg/(cm³ d)), ZIF-8 (267 kg/(cm³ d)) and Co-ZIF-8 (160 kg/(cm³ d)) in a single microreactor, respectively. It paves the way to massively produce ZIFs without scale-up effect. All the ZIFs obtained from microreactions had high crystallinity except ZIF-67. ZIF-7 synthesized in these conditions showed a typical monoclinic *C2/c* ZIF-7 phase respect to the existence of water in the mixture solvents, which drove the structure from porous phase into the dense phase of monoclinic *C2/c* ZIF-7. ZIF-8 and Co-ZIF-8 both exhibited sodalite structure respect to the tetra coordination properties of Zn^{2+} and Co^{2+} . The small polyhedron ZIF-8 particles had grown into large cubic particles with reaction time increased to 5 min. The Co doping exhibited strong effect on the particles' morphology. The Co-ZIF-8 prepared from low concentration reactants showed spherical octadecahedron morphology, where {110} surfaces were the main surface. On the contrary, the high concentrated reactants resulted in cubic octadecahedron, where the {100} were mainly occupied the surface. The reason could be that the pure Co was difficult to form ZIF-67 in this condition; therefore the Co changes the formation of ZIF-8. Accordingly, this work provides a facile approach to massively produce diverse ZIFs with controllable morphology in microfluidic system.

zeolitic imidazolate frameworks, droplet microfluidic reactor, continuous flow synthesis, process intensification, massive production

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