

四苯基甲烷球磨法合成多孔碘蒸气吸附材料

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摘要:【目的】避免在核能利用过程中产生的常见放射性污染核素¹²⁹I和¹³¹I等碘蒸气泄漏对环境和生物产生危害,制备并探讨具有丰富孔道的有机多孔聚合物对碘蒸气的吸附性能。【方法】采用简便快捷的机械合成法,以具有正四面体结构的四苯基甲烷为单体,利用高能行星式球磨机球磨2 h制备3种具有较大比表面积和丰富孔道的有机多孔聚合物T-FDA、T-DCM和T-DCE,并利用碘单质在温度为75℃的密闭体系内升华模拟放射性碘蒸气,分别测试3种多孔材料的碘蒸气吸附性能。【结果】T-FDA、T-DCM、T-DCE的碘蒸气吸附质量分数分别可达461%、486%、444%,达到饱和吸附量的时间分别为5、8、6 h,且多孔材料在循环使用5次后碘吸附性能仅有轻微下降(≤6.8%)。【结论】以四苯基甲烷为单体,通过快速球磨法合成的多孔材料具有良好的碘蒸气吸附性能,有望在放射性碘蒸气吸附领域发挥重要作用。

关键词: 四苯基甲烷; 球磨法; 有机多孔材料; 碘蒸气吸附

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核能是当前应用较为广泛、技术较为成熟的高效清洁能源之一,具有清洁低碳、经济高效、能量密度高等优点,但是在实际应用当中,如何更安全地利用核能始终是人类面临的重要问题^[1]。当前较为成熟的技术是通过核裂变反应从原子核释放能量,用于发电等民生、军事用途,然而在利用核能过程中也会产生放射性污染核素。放射性碘是重要的放射性污染物之一,主要来源为核工业、医疗废物泄漏。放射性碘主要包括¹²⁹I、¹³¹I等同位素,绝大部分会以气体形式释放,对人类健康和环境造成威胁^[2]。¹²⁹I会与其他元素形成化合物,造成环境永久性污染,¹³¹I会通过食物链和大气循环被人体吸收并富集于甲状腺内,严重威胁甲状腺正常功能^[3]。放射性碘同位素半衰期可长达 1.6×10^7 a,气化温度低(75℃),自然环境中流动性强,危害性不能忽视。如何妥善处理放射性碘是当前研究者关注的重要问题,其中利用多孔材料吸附碘蒸气是有效的解决方法之一^[4]。

传统的多孔碘吸附剂,如活性炭^[5]和多孔沸石^[6]等,虽然具有生产工艺成熟、成本低廉等优点,但这些材料仍然存在密度较大、结构功能有限、比表面积较小、孔道尺寸较大、吸附容量不高、循环性能不佳等缺点,在实际工业应用方面受到较大限制。

有机多孔聚合物(porous organic polymers, POPs)是近些年来兴起的一类新型多孔材料,POPs材料的物理化学稳定性高、密度小、孔隙率和比表面积大、吸附性能优异、可循环利用等优点,在放射性碘

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的治理领域具有良好的应用前景^[7]。特别是 POPs 材料由纯有机元素组成,与传统无机类多孔材料相比具有合成策略多样、结构可调节、成本低廉等优势^[8],因此受到科研工作者的广泛关注并已成功应用于碘蒸气吸附领域。例如,Zhai等^[9]合成了2种含有甲氧基官能团且比表面积大、化学稳定性优良的新型共价有机骨架,碘蒸气吸附容量分别3.21、5.07 g/g。Chang等^[10]报道了2种四硫脲基共价有机框架(COFs) JUC-560和JUC-561,并对二者的碘吸附性能进行研究,所得材料比表面积可高达2 359 m²/g,同时表现出极佳的碘吸附性能(JUC-561碘吸附容量高达8.19 g/g)。宋玲等^[11]合成了2种三嗪基多孔有机聚合物 COP-1和COP-2,对碘蒸气的吸附量分别为1.60和2.13 g/g,并通过实验证明了碘吸附机制主要为物理吸附。Zou等^[12]合成了2种含有不同长度炔键的类金刚石三维有机多孔材料CPOF-2和CPOF-3,挥发性碘吸附容量可高达5.87 g/g。Liu等^[13]基于Tröger碱合成了具有三维刚性六连通结构的多孔三萜烯网络TB-PTN,比表面积可达1 528 m²/g,碘蒸气吸附质量分数高达240%。Hassan等^[14]基于六氯环三磷腈单体合成的HPOP-4,碘蒸气吸附容量高达6.25 g/g且具有良好的重复利用性。综上所述,具有大比表面积、高孔隙率且具有稳定刚性多孔框架结构的POPs材料非常适用于碘蒸气吸附,然而许多材料为达到较好的碘蒸气吸附性能,需要选择特定合成方法或使用特殊结构单体来构建,且往往使用大量有机溶剂并加热数小时至数天不等^[8],间接增加了合成成本,材料实际应用的可能性受到较大限制。

球磨机是工业上常见的破碎设备之一,广泛用于选矿、建材及化工等行业^[15]。此外,研究者也将球磨机用于化学合成,这种机械合成方法具有反应时间短、效率高、简便易行等优势,具备大规模工业化生产的潜力^[16]。本文中以具有正四面体结构的四苯基甲烷为单体,以高能行星式球磨机为反应器,通过成本低廉、简便易行的合成方法快速、高效构建3种具有丰富孔道结构的POPs材料;对球磨法合成的多孔材料进行物理化学结构表征,并通过模拟放射性碘蒸气环境,测试材料对碘蒸气的吸附性能及循环利用性,为POPs材料的大规模生产和实际碘蒸气吸附应用提供可行的方案。

1 材料与方法

1.1 试剂材料和仪器设备

试剂材料:四苯基甲烷(质量分数为98%,安耐吉化学试剂有限公司)、二甲氧基甲烷(FDA,质量分数为98%,阿拉丁生化科技股份有限公司);二氯甲烷、1,2-二氯乙烷、无水三氯化铁、无水三氯化铝(均为分析纯,国药集团化学试剂有限公司)。上述所有实验试剂均可直接使用,无需进一步纯化处理。

仪器设备:PULVERISETTE-4型可变转速比率高能行星式球磨机(德国Fritsch公司);Vertex 70型傅里叶变换红外光谱分析仪(FTIR,德国Bruker公司);¹³C CP/MAS型固态核磁(400 MHz WB,德国Bruker公司,Advance II);HITACHI SU8010型场发射扫描电镜(FE-SEM,日本日立公司);JEM-2100 PLUS型场发射透射电镜(FE-TEM,日本电子株式会社);TGA8000型热重分析仪(TGA,美国Perkin-Elmer公司);Micromeritics ASAP 2020型吸脱附等温线和孔径分布吸附仪(美国Micromeritics公司)。

1.2 多孔碘吸附材料制备

四苯基甲烷—二甲氧基甲烷交联材料(T-FDA):称取质量为0.32 g的四苯基甲烷,质量为0.912 g的交联剂FDA和质量为1.95 g的无水三氯化铁,量取体积为10 mL的溶剂1,2-二氯乙烷,先后加入到已放有50个直径为10 mm氧化锆微球的250 mL氧化锆研磨罐中,通入氩气保护5 min之后封紧罐盖。设置行星式高能球磨机的公转速度和自转速度均为400 r/min,室温下球磨工作2 h后停止。球磨罐小心打开后,加入100 mL无水甲醇淬灭反应体系并转移,用甲醇和氯仿分别抽滤洗涤数次后得到棕色粉体产物。最后将产物置于温度为60 °C的真空烘箱中干燥24 h。所得材料命名为T-FDA。

四苯基甲烷—二氯甲烷交联材料(T-DCM):称取0.32 g四苯基甲烷和1.6 g无水三氯化铝,量取10 mL溶剂(兼作交联剂)二氯甲烷,球磨合成过程及相关参数与上述T-FDA材料相同。在小心打开球磨罐后,加入100 mL无水乙醇淬灭反应体系并转移,用乙醇和氯仿分别抽滤、洗涤数次后得到棕褐色粉体产物。最后产物干燥过程与T-FDA相同,所得材料命名为T-DCM。

四苯基甲烷—1,2-二氯乙烷交联材料(T-DCE):称取0.32 g四苯基甲烷和1.6 g无水三氯化铝,量

取 10 mL 溶剂(兼作交联剂)1,2-二氯乙烷,球磨合成过程及相关参数与上述 T-FDA 和 T-DCM 材料相同。将球磨罐小心打开后,加入 100 mL 无水乙醇淬灭反应体系并转移,用质量分数为 5% 的稀盐酸、乙醇和氯仿分别抽滤、洗涤数次后得到深褐色粉体产物。最后产物干燥过程与 T-FDA 和 T-DCM 相同,所得材料命名为 T-DCE。

1.3 对碘蒸气的吸附

碘蒸气吸附实验具体操作过程如下:精确称量 0.2 g 多孔材料粉末放入预先称重的边长为 25 mm 的正方体小样品瓶中,再称取 2 g 碘单质加入另一个样品瓶,将 2 个样品瓶放入玻璃容器中形成密闭体系。之后将密封好的密体系置于 75 °C 恒温烘箱内,使粉体样品置于饱和碘蒸气环境当中,在固定的时间节点(1、2、3、4、5、6、8、12、16、20、24 h)取出密闭容器并快速冷却,取出装有粉末样品的样品瓶并精确称量其质量。

2 结果与分析

2.1 材料基本结构分析

四苯基甲烷分子中含有芳环结构,在催化剂和球磨条件作用下,单体通过交联剂连接后形成具有丰富孔道的多孔聚合物,如图 1 所示。

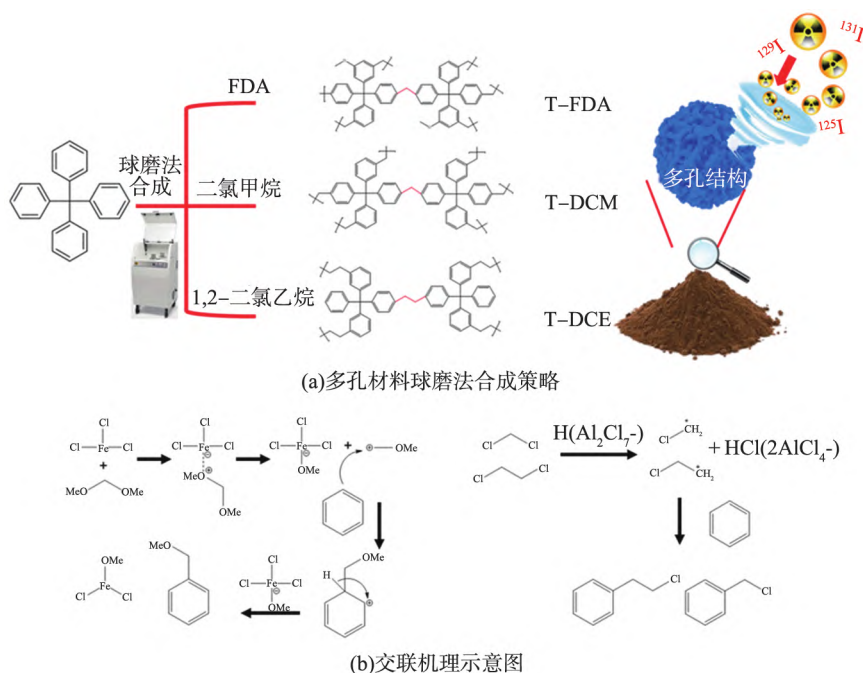


图1 多孔材料球磨法合成策略及交联机制示意图

Fig. 1 Ball-milling synthetic strategy of porous materials and schematic diagram of cross-linking mechanism

图2所示为多孔材料T-FDA、T-DCM、T-DCE的FTIR谱图和固态核磁共振谱图。球磨法所合成3种材料的FTIR光谱如图2(a)所示,在FTIR光谱中,波数为3 000~2 800 cm^{-1} 处存在明显的亚甲基C—H振动特征峰,表明材料结构中具有大量的亚甲基($-\text{CH}_2-$)存在^[17]。四苯基甲烷单体中并不存在此类结构,由此可判定多孔固体产物中的亚甲基结构来源于交联剂,通过傅克烷基化反应将不同单体通过亚甲基连接并成功构建多孔结构骨架。所有材料在波数为1 440 cm^{-1} 处呈现出亚甲基连接体 $-\text{CH}_2-$ 弯曲模式的特征峰,同时在波数分别为1 420、1 260 cm^{-1} 处呈现出 $\text{Cl}-\text{CH}_2$ 的弯曲和摆动的特征峰,说明材料中均有一定的氯元素残留,可能来自于催化剂或未完全反应的含氯交联剂^[18]。同样地,3种材料在波数为1 650~1 450 cm^{-1} 处存在芳环的骨架伸缩振动峰,在波数为900~650 cm^{-1} 处均出现较为明显的芳环面外弯曲振动吸收峰^[19]。在波数分别为600、800 cm^{-1} 处出现的峰是由于芳环上1、4位置取代所致,说明3种材料中亚甲基与苯环桥联的位置主要以单体中苯环与季碳原子连接位置的对位为主(图1

结构示意图中红色线段所示)。特别地,对于T-FDA,在波数为 $1\,100\text{ cm}^{-1}$ 处存在明显的C—O—C弯曲振动峰,这是由于交联剂二甲氧基甲烷在球磨过程并未完全反应,残存有C—O—C结构所致^[20]。此外,通过固态核磁共振谱图(图2(b))可见,在化学位移 δ 为 142×10^{-6} 和 132×10^{-6} 处出现明显的特征峰,分别代表四苯基甲烷中苯环上发生化学交联反应的碳原子和未发生化学交联反应的碳原子,同时 δ 为 37×10^{-6} 处的特征峰属于连接单元亚甲基碳原子,证明单体之间通过交联剂形成的亚甲基互相连接从而形成多孔骨架结构^[21]。 δ 为 60×10^{-6} 处的特征峰属于四苯基甲烷中的季碳原子, δ 为 18×10^{-6} 处的峰属于材料结构中残存的甲基($-\text{CH}_3$)^[22]。

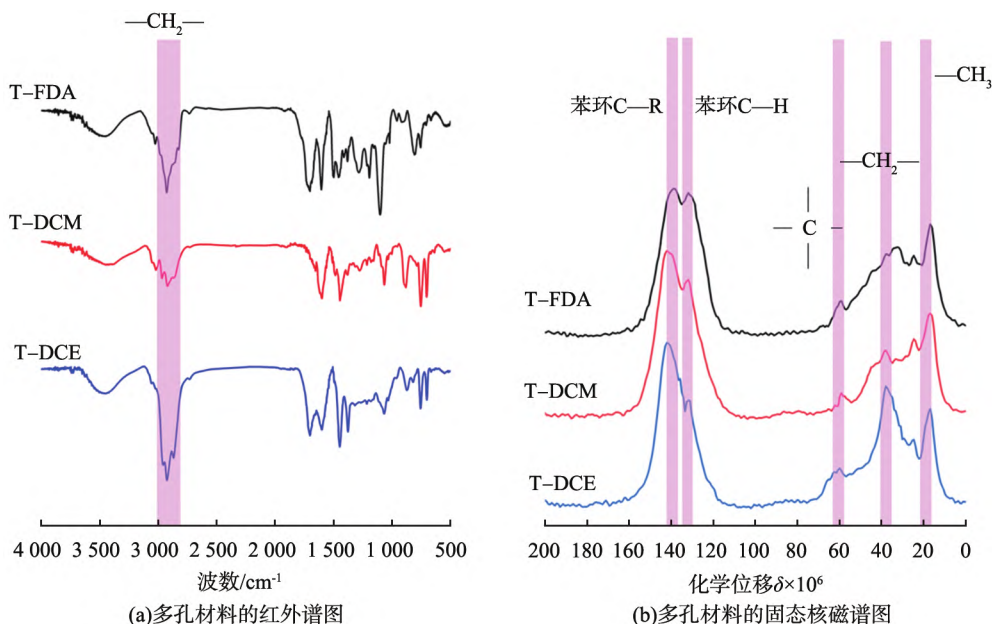


图2 多孔材料T-FDA、T-DCM、T-DCE的FTIR谱图和固态核磁共振谱图

Fig. 2 FTIR and solid-state NMR spectra of porous materials T-FDA, T-DCM and T-DCE

3种多孔材料的形貌特征通过场发射扫描电子显微镜观察。图3所示为多孔材料T-FDA、T-DCM、T-DCE的FE-SEM图像。由图3(a)中可见,以二甲氧基甲烷(FDA)为交联剂球磨合成的T-FDA,其形貌主要为微米级的块体,表面呈现较为松散的微颗粒聚集状态。而T-DCM和T-DCE 2个样品没有明显的形貌差异,虽然在扫描电镜下也主要表现为微米级的块体形貌,但是二者的表面相对较为致密,这有可能与所使用的交联剂及化学反应过程不同所致。本实验中通过球磨法制备的多孔材料与通过传统溶剂热方法合成的多孔材料具有相似的形貌特点,即:使用FDA作为交联剂合成的多孔材料大多呈现类似颗粒状、珊瑚状的疏松质地形貌,在电镜图片中可以观察到具有许多颗粒堆积形成的介孔和大孔;而使用氯代烷烃(如二氯甲烷等)作为交联剂合成的多孔材料则呈现质地紧密、表面平整的块体,甚至可构建具有特殊二维层状形貌的材料^[18]。

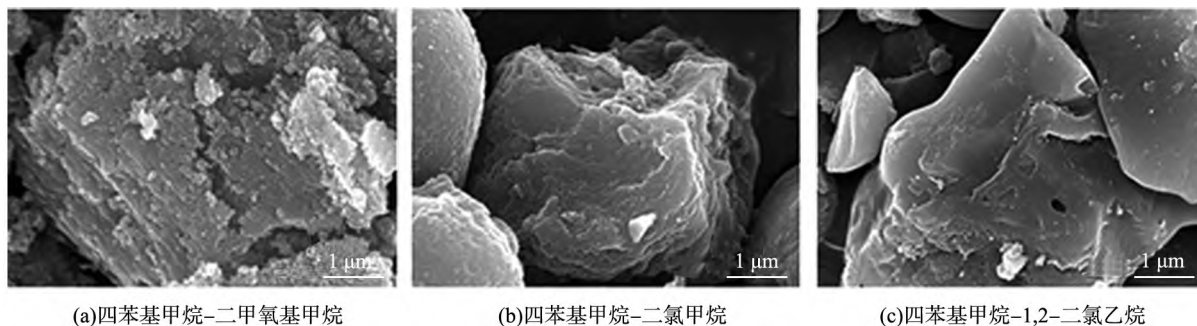


图3 多孔材料T-FDA、T-DCM、T-DCE的FE-SEM图像

Fig. 3 FE-SEM images of porous materials T-FDA, T-DCM and T-DCE

多孔材料的微观孔道结构特征通过分辨率更高的FE-TEM观察。图4所示为T-FDA、T-DCM、T-DCE的FE-TEM图像。3种多孔材料在透射电镜下均可观察到大量的细微孔道存在,说明与传统的溶剂热方法相比,所需时间更短的球磨法所制备的多孔材料内部孔道仍很丰富,并且同样具有稳定的结构,在透射电镜长时间高能电子束照射下不会被破坏。

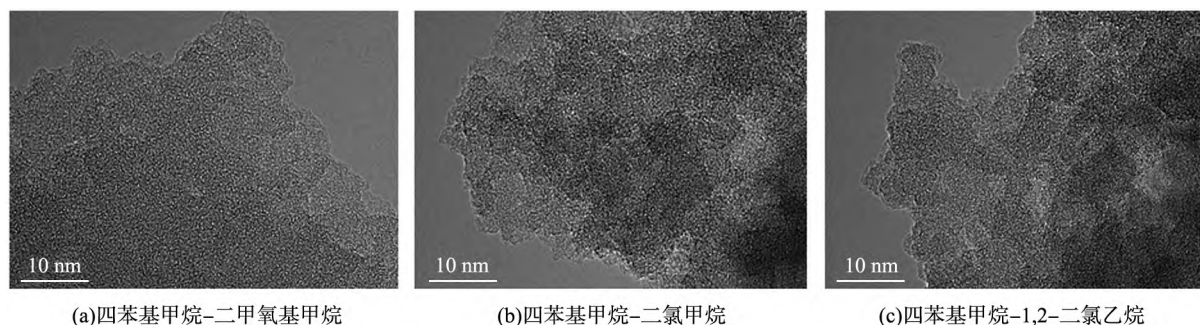


图4 多孔材料T-FDA、T-DCM、T-DCE的FE-TEM图像

Fig. 4 FE-TEM images of porous materials T-FDA, T-DCM and T-DCE

多孔材料结构的热稳定性通过TGA表征。图5所示为3种材料在氮气气氛中的TGA曲线。在从室温逐渐升至800℃的过程中,3种材料残余质量随温度变化的规律有明显的差异。当升温超过150℃时,T-FDA材料的热重曲线出现断崖式下降,说明此材料的部分组分发生分解;当温度超过225℃时,T-FDA质量下降趋势逐渐放缓,直至温度达到800℃过程中T-FDA的质量呈现缓慢下降趋势。结合图3中T-FDA的形貌特点来看,这有可能是由于大量尺寸微小且呈松散颗粒状的T-FDA在较低温度下首先发生了热分解所导致的。而与T-FDA相比,T-DCM和T-DCE的热重曲线则表现出明显差异,差异之处在于T-DCM和T-DCE的质量均随着温度的逐渐升高缓慢降低,未出现断崖式下降,这与二者相对致密的块体形貌有一定的关系;其中T-DCM在300℃以下的升温区间内热稳定性优于T-DCE,在超过300℃之后其质量损失要比T-DCE略大。在达到终点温度800℃后,T-FDA、T-DCM、T-DCE的最终残余质量分别为58.8%、54.1%和62.6%。

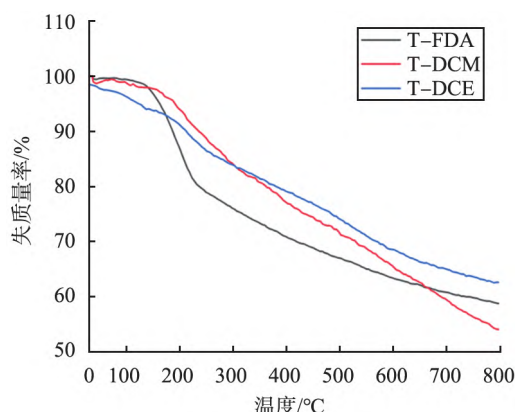


图5 T-FDA、T-DCM、T-DCE的TGA曲线(氮气气氛)

Fig. 5 TGA profile of T-FDA, T-DCM and T-DCE(N_2 atmosphere)

多孔材料的孔道特性利用比表面积和孔径吸附仪表征,结果如表1所示。图6所示为T-FDA、T-DCM、T-DCE的 N_2 吸附-脱附等温线以及对应的孔径分布图。结合表1中各材料的相关孔道特征数据可见,对于单体四苯基甲烷,虽然常温常压状态下为粉末状态,但是不存在任何可检测到的孔道;极小的比表面积数值可能是松散粉末堆积所致。而将单体与不同交联剂、催化剂混合球磨反应2 h后,所得多孔材料T-FDA、T-DCM和T-DCE的比表面积分别为398、516、753 m^2/g , N_2 吸附-脱附等温线均表现为IV型曲线,在低压条件下(相对压力 $p/p_0 < 0.1$, p 为测试体系当前 N_2 压力值, p_0 为标准大气压) N_2 吸

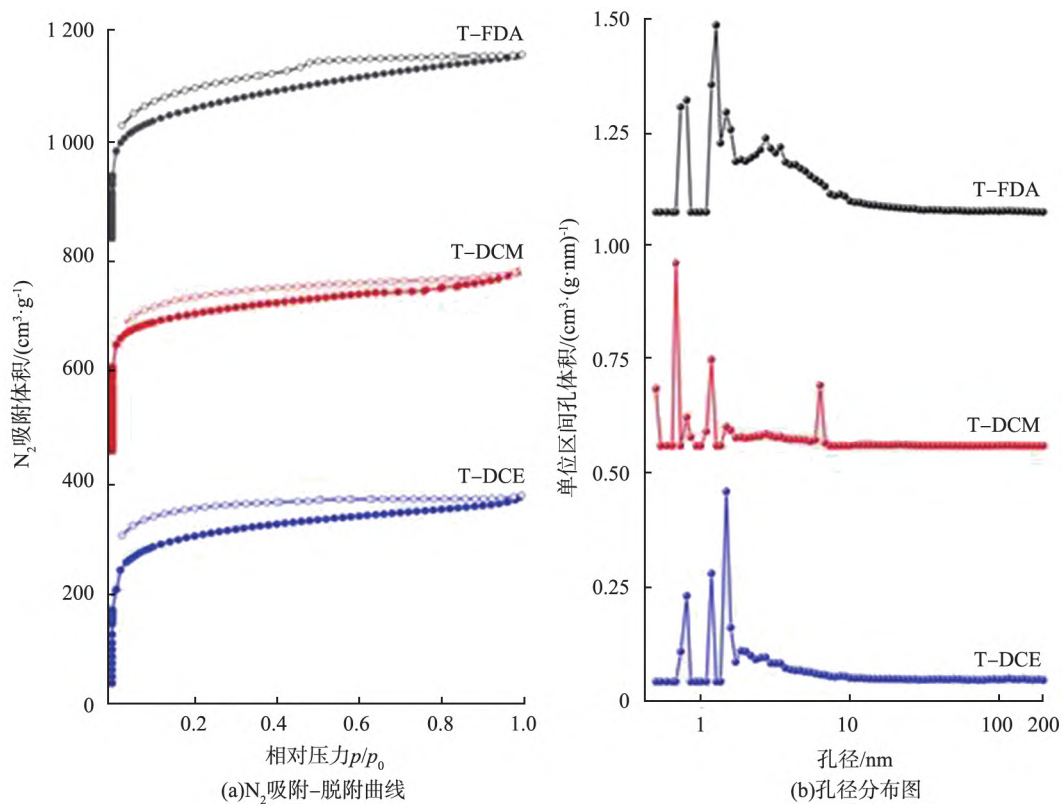
附曲线上升较快,说明3种多孔材料中均含有大量的微孔结构;曲线中段出现的回滞环表明材料中存在一定的介孔;而高压区范围内($p/p_0=0.8\sim 1.0$)吸附曲线未见明显上升,表明3种多孔材料中大孔的比例极低。上述特征从图6(b)的孔径分布曲线中明显可见,虽然T-FDA、T-DCM、T-DCE 3种多孔材料均含有大量的微孔,但T-FDA的孔径为2~10 nm的介孔数量略多于T-DCM和T-DCE,T-DCM和T-DCE的孔径主要分布区间为小于2 nm,大多数为微孔甚至是超微孔(孔径 ≤ 0.7 nm),其中T-DCE的孔径大于2 nm的介孔比例较T-DCM略多。由以上分析可知,丰富的微孔甚至是超微孔结构决定了T-FDA、T-DCM、T-DCE 3种材料具有较大的比表面积,而大比表面积和连续分布的孔道又决定了材料理论上具有优异的吸附特性。鉴于多孔材料在物质吸附领域尤其是气体物质的吸附与分离方面具有独特的应用优势,因此将上述3种材料用于碘蒸气吸附(以常规碘蒸气模拟放射性碘蒸气)并测试其吸附性能。

表1 材料的孔道特性

Tab. 1 Porosity properties of materials.

样品名称	BET 比表面积/($\text{m}^2\cdot\text{g}^{-1}$)	Langmuir 比表面积/($\text{m}^2\cdot\text{g}^{-1}$)	总孔体积/($\text{cm}^3\cdot\text{g}^{-1}$)	微孔体积/($\text{cm}^3\cdot\text{g}^{-1}$)
四苯基甲烷单体	3			
T-FDA	398	530	0.22	0.14
T-DCM	516	763	0.24	0.19
T-DCE	753	902	0.25	0.12

注: BET比表面积通过BET方程在热力学温度为77.3 K下的 N_2 吸附等温线计算所得; Langmuir比表面积通过Langmuir方程在热力学温度为77.3 K下 N_2 吸附等温线计算所得; 总孔体积通过 $p/p_0=0.995$ 处的 N_2 吸附量计算所得; 微孔体积通过 $p/p_0=0.050$ 处的 N_2 吸附量计算所得。T-FDA为四苯基甲烷—二甲氧基甲烷交联材料, T-DCM为四苯基甲烷—二氯甲烷交联材料, T-DCE为四苯基甲烷—二氯乙烷交联材料。

图6 T-FDA、T-DCM、T-DCE的 N_2 吸附-脱附曲线和孔径分布图Fig. 6 N_2 adsorption-desorption isotherms and pore size distribution of T-FDA, T-DCM and T-DCE

2.2 有机多孔材料的碘蒸气吸附实验结果

采用重量差法来计算样品在不同时刻的碘蒸气吸附量,计算式为

$$w_t = \frac{m_t - m_0}{m_0} \times 100\%, \quad (1)$$

式中: w_t 为碘蒸气吸附质量分数; m_t 为样品吸附碘后 t 时刻的质量; m_0 为样品的初始质量。

图7所示为T-FDA、T-DCM、T-DCE的粉体状态以及吸附碘蒸气饱和后的粉体状态图, T-FDA、T-DCM、T-DCE吸附碘蒸气后颜色变化比较明显,在吸附碘蒸气饱和后颜色均呈现棕黑色,表明3种多孔材料对碘蒸气均具有明显的吸附效果。

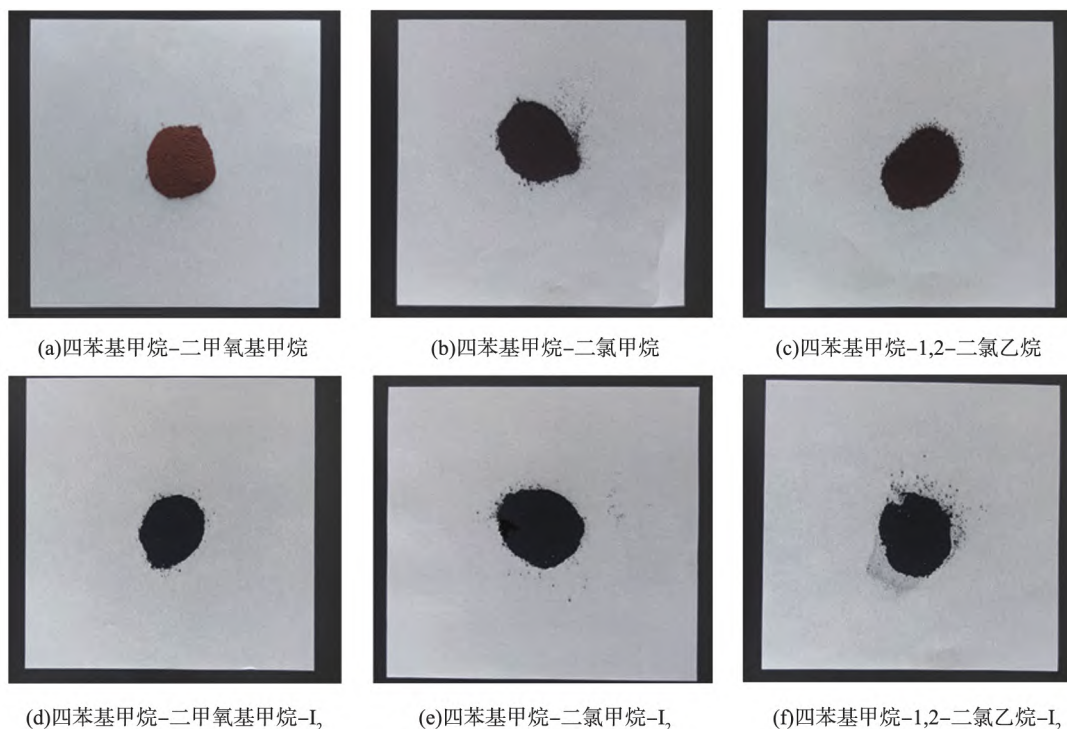


图7 T-FDA、T-DCM、T-DCE的粉体状态以及吸附碘蒸气饱和后的粉体状态

Fig. 7 Powder state of T-FDA, T-DCM and T-DCE, and powder state after saturated adsorption of iodine vapor

图8所示为T-FDA、T-DCM、T-DCE的碘蒸气吸附质量分数与时间关系曲线图。由图可以看出,3种多孔材料均可在8 h内达到最大吸附量并保持平衡。T-FDA吸附速率相对最快,在5 h后可达到最大吸附质量分数461%;而T-DCM碘蒸气吸附饱和时间相对较长,但吸附质量分数相对较大,在8 h之后可达到486%;T-DCE则在6 h吸附碘蒸气达到最大吸附质量分数444%。从图8(d)比较可见,T-DCM吸附量相对最大,达到饱和的时间也相对较长。结合表1来看,这可能是由于材料自身的微孔和极微孔数量较多、在孔道中所占的比例较大,对碘蒸气的吸附能力相对较强,吸附量也较大,但是碘蒸气分子充分进入微孔和极微孔所需时间较长。T-FDA达到碘蒸气吸附饱和的速率虽快,但是吸附质量分数(461%)不及T-DCM。而T-DCE虽然比表面积最大,但是其微孔所占比例最低,T-DCE对碘蒸气的吸附效果相对最弱,吸附质量分数相对也最小(444%)。由图可以看出,3种物质吸附速率的差异主要由孔道分布的不同所致,吸附质量分数与微孔比例的成正比规律较为明显。除微孔之外,3种材料中均含有一定比例的介孔和大孔,这些多级孔道也有利于碘分子的扩散和传输。由于材料中基本不含有碳氢之外的其他杂元素,因此材料对碘蒸气主要通过孔道(尤其是尺寸较小的微孔)进行物理吸附。

此外,本文中还对3种多孔材料的循环使用性进行了探索和分析。根据已有相关文献报道,采用乙醇洗脱的方法可以充分移除多孔材料中吸附的碘^[23]。在每次碘蒸气吸附实验结束并称重后,将吸附碘蒸气饱和后的样品用滤纸包好放到索氏提取器中,使用无水乙醇反复索提清洗48 h以上,直至回流溶液澄清为止。脱附后的样品经过温度为60 °C真空干燥24 h后,回收并进行下一次碘蒸气吸附实验。图9所示为3种材料脱附再生与循环性能的测试结果,对每种材料进行5次碘蒸气吸附-乙醇洗脱循环利用实验,每个样品重复5次得到图示结果。由图可知,T-FDA在循环使用5次后吸附效率仅有轻微下

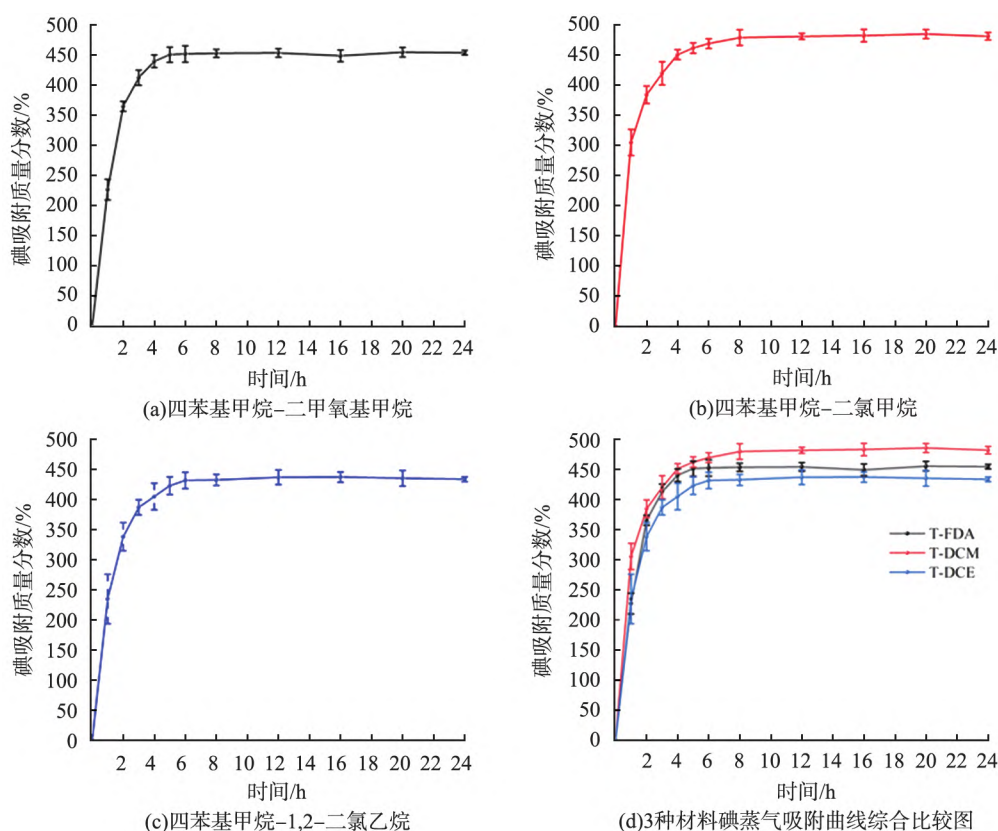


图8 T-FDA、T-DCM、T-DCE的碘蒸气吸附质量分数与时间关系曲线

Fig. 8 Time dependent curves of mass of gaseous iodine adsorbed by T-FDA, T-DCM and T-DCE

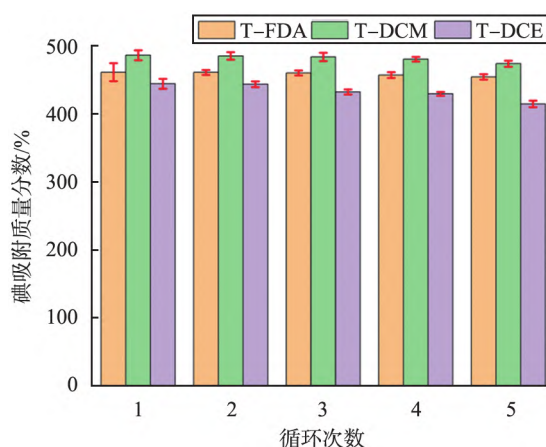


图9 T-FDA、T-DCM、T-DCE的碘蒸气吸附循环使用图

Fig. 9 Iodine vapor adsorption recycling of T-FDA, T-DCM and T-DCE

降,碘蒸气吸附质量分数由第1次的461%下降至第5次的454%,下降幅度仅有1.5%; T-DCM的碘蒸气吸附质量分数由首次的486%下降至第5次的473%,下降幅度为2.7%; T-DCE的碘蒸气吸附质量分数由首次的444%下降至第5次的414%,下降幅度为6.8%。由此可见,通过球磨法合成得到的3种多孔材料的循环利用性较好,循环使用5次后吸附效率仅有轻微降低。

表2所示为近些年部分文献报道的各类多孔材料对碘蒸气的吸附质量分数。通过比较可见,采用球磨法合成的T-FDA、T-DCM、T-DCE与其他已报道的碘蒸气吸附材料相比,碘蒸气吸附性能表现较好。本文中材料的合成过程简便快捷,避免了传统溶剂热合成法对能源和有机溶剂的大量使用,具有能耗小、成本低的优势。

表2 与其他材料的碘蒸气吸附性能比较表

Tab. 2 Comparison of iodine vapor adsorption performance with other materials.

序号	碘蒸气吸附材料	比表面积/($\text{m}^2 \cdot \text{g}^{-1}$)	吸附实验环境温度/ $^{\circ}\text{C}$	吸附质量分数/%	文献
1	CTFs	1 476	75	431.0	[24]
2	HCP6	30	78	324.8	[25]
3	TAPA-PDA COF	685	77	509.0	[26]
4	$\text{NH}_2\text{-UiO-66@Br-COFs}$	966	75	373.0	[27]
5	PAPOA-N(CH_3) ₂	1 444	75	356.0	[28]
6	USTB-1c	1 454	75	580.0	[29]
7	NLHCP-2	444	78	250.0	[30]
8	C6-TRZ-TPA COF	1 058	75	483.2	[31]
9	PTZ-TPC-MA	132	75	198.1	[32]
10	Ag0-BILP-101	232	80	370.0	[33]
11	T-FAD	398	75	461.0	本文
12	T-DCM	516	75	486.0	本文
13	T-DCE	753	75	444.0	本文

3 结论

1)采用球磨合成法,以具有立体结构的四苯基甲烷分子为构建单元,通过3种不同的交联策略,球磨2 h合成了T-FDA、T-DCM、T-DCE 3种多孔材料,比表面积分别为398、516、753 m^2/g ,同时具有丰富的微孔和连续的多级孔道分布,结构较为稳定。

2)将T-FDA、T-DCM、T-DCE 3种多孔材料应用于碘蒸气吸附,在温度为75 $^{\circ}\text{C}$ 的密闭体系中以常规碘单质模拟放射性碘的蒸气挥发环境,3种多孔材料的碘吸附质量分数分别可达461%、486%和444%,可以循环重复使用多达5次,且性能仅略微下降。

3)绝大多数有机多孔材料的碘蒸气吸附质量分数在200%~600%之间,相比之下,T-FDA、T-DCM、T-DCE 3种多孔材料的碘蒸气吸附量与同类有机多孔材料相比处于较高水平,同时通过球磨法合成多孔材料具有时间短、效率高、能耗低等优点,避免了能源和有机溶剂的大量消耗和使用,具有一定的工业化大规模生产潜力,为有机多孔材料在碘蒸气吸附领域的实际应用提供了新的参考思路。

利益冲突声明(Conflict of Interests)

所有作者声明不存在利益冲突。

All authors disclose no relevant conflict of interests.

作者贡献(Author's Contributions)

张承昕和王余莲进行了方案设计和论文写作,苏峻樟、董春阳、王浩然和肖坤富进行合成实验与表征,袁志刚和苏德生参与了论文的修改。所有作者均阅读并同意了最终稿件的提交。

The study was designed by ZHANG Chengxin and WANG Yulian, who also conducted paper writing. While SU Junzhang, DONG Chunyang, WANG Haoran, and XIAO Kunfu conducted synthesis experiments and characterization. YUAN Zhigang and SU Desheng participated in the revision of the paper. All authors have read the last version of paper and consented for submission.

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Ball-milling synthesis of organic porous materials with tetraphenylmethane for iodine vapor adsorption

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Abstract

Objective Radioactive isotopes of iodine, such as iodine-129 and iodine-131, are prevalent contaminants during nuclear energy utilization. Managing radioactive iodine is a critical concern for researchers and the use of porous materials for iodine vapor adsorption presents a promising solution. However, traditional porous iodine adsorbents, including activated carbon and porous zeolite, exhibit drawbacks such as high density, limited structural versatility, low specific surface area, large pore size, low adsorption capacity, and inadequate cycling performance, significantly impeding their industrial applicability. Given these challenges, it is necessary to develop novel porous materials for efficient iodine vapor adsorption. Porous Organic Polymers (POPs) emerge as a potential solution, characterized by high physical and chemical stability, low density, high porosity, large specific surface area, outstanding adsorption performance, and recyclability, offering a promising prospects in radioactive iodine treatment. Ball mills, as common crushing equipment, find widespread application in industries such as mineral processing, building materials, and chemical industry. Furthermore, researchers use ball mills for chemical synthesis due to their advantages such as brief reaction times, high efficiency, simplicity, and potential for low-cost, straightforward, large-scale industrial production. In this study, tetraphenylmethane, featuring a three-dimensional structure served as the monomer, while a high-

energy planetary ball mill functioned as a reactor, enabling swift and efficient construction of three POPs materials. These materials were evaluated for their adsorption performance and recycling ability in a simulated radioactive iodine vapor environment. Our research offers a viable solution for large-scale production of POPs materials and their practical application in iodine vapor adsorption.

Methods In this study, we successfully synthesized three distinct porous organic polymers (POPs), namely T-FDA, T-DCM, and T-DCE, utilizing a rapid and efficient ball milling approach. This method resulted in materials characterized by high specific surface area and abundant pore structure. The synthesis process involved employing tetraphenylmethane as a three-dimensional structure monomer, along with either anhydrous ferric chloride or anhydrous aluminum trichloride as catalysts, and three different crosslinking agents (dimethoxymethane, dichloromethane, and 1,2-dichloroethane) to generate the aforementioned POPs materials. The synthesis procedure commenced by introducing the requisite reagents into a 250 mL zirconia grinding jar containing 50 zirconia spheres (Diameter: 10 mm). After purging the jar with an argon atmosphere and sealing it, the planetary high-energy ball mill was set to a revolution speed and rotation speed of 400 r/min, with the milling process lasting for 2 hours at room temperature. Subsequently, the iodine vapor adsorption capacity of the porous materials was evaluated. Specifically, 0.2 g of POPs powders were accurately weighed and placed into a pre-weighed small sample bottle while 2 g of iodine was introduced into another sample bottle. These two bottles were then positioned within a glass container to create a sealed system, which was subsequently transferred into an oven set at 75 °C to expose the powder to a saturated iodine vapor environment. At predetermined time intervals (1, 2, 3, 4, 5, 6, 8, 12, 16, 20, and 24 hours), the sealed container was removed from the oven and rapidly cooled, following which the mass of the sample bottle was accurately determined.

Results and Discussion The resulting porous materials, T-FDA, T-DCM, and T-DCE, exhibited high specific surface area (398, 516, and 753 m²/g respectively), abundant pore channels, and excellent structural stability. These materials were characterized by a significant presence of micropores (<2 nm) and even ultra-micropores (<0.7 nm), alongside a certain proportion of mesopores. The interconnected nature of these pores gave unique advantages to the materials, particularly in the realm of adsorption, notably in the adsorption and separation of gas substances such as radioactive iodine vapor. Based on experimental findings, the iodine adsorption capacity of T-FDA, T-DCM, and T-DCE could reach up to 461%, 486%, and 444% respectively. These materials achieved adsorption saturation at the 5th, 8th, and 6th hour respectively. Furthermore, to assess the materials' cycling performance, iodine vapor adsorption recycling experiments were conducted five times for each of T-FDA, T-DCM, and T-DCE. The results indicated that the iodine vapor adsorption efficiency of T-FDA only slightly decreased after five cycles of use, with the iodine vapor adsorption amount reducing from 461% initially to 454% after the fifth cycling, representing a decrease of only 1.5%. For T-DCM, its iodine vapor adsorption capacity decreased from 486% in the first time to 473% in the fifth time, corresponding to a reduction of 2.7%. Similarly, the iodine vapor adsorption of T-DCE decreased from 444% in the first time to 414% in the fifth time, with a reduction of 6.8%. Notably, the iodine adsorption performance of the three porous materials only slightly decreased after five cycles of use.

Conclusion In this study, utilizing the ball-milling method, three porous materials (T-FDA, T-DCM, and T-DCE) were synthesized within a remarkably short period of 2 hours. Subsequently, structural analyses and iodine vapor adsorption performance of these materials were conducted. Our findings revealed that T-FDA, T-DCM, and T-DCE exhibited specific surface areas of 398, 516, and 753 m²/g, respectively. These materials showcased abundant micropores, continuous multi-level pore distribution, and a relatively stable structure. To assess their practical utility, we applied these porous materials to iodine vapor adsorption in a closed system operating at 75 °C, simulating the vapor evaporation environment of radioactive iodine with standard iodine elements. The experimental outcomes demonstrated impressive iodine adsorption mass fractions of 461%, 486%, and 444% for T-FDA, T-DCM, and T-DCE, respectively. Remarkably, these materials exhibited reusability for up to 5 cycles with only a marginal decrease in performance (≤6.8%). Our results underscore the exceptional iodine vapor adsorption performance of the porous materials synthesized via fast ball milling, suggesting their potential significance in the context of radioactive iodine adsorption. Moreover, the ball milling synthetic method offers advantages including short reaction time, high efficiency, low energy consumption, and avoidance of extensive energy and organic solvent usage, thereby harboring considerable potential for large-scale industrial production.

Keywords: tetraphenylmethane; ball-milling method; porous organic polymer; iodine vapor adsorption

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