

# 溶胶-凝胶辅助水热双模板法制备球形介孔 $\text{TiO}_2$

王殿平, 刘守新\*

东北林业大学生物质材料教育部重点实验室, 黑龙江哈尔滨 150040

WANG Dianping, LIU Shouxin\*

Key Laboratory of Bio-based Material of Science and Technology of Ministry of Education, Northeast Forestry University, Harbin 150040, Heilongjiang, China

- 摘要
- 参考文献
- 相关文章

Download: PDF (1446KB) HTML (1KB) Export: BibTeX or EndNote (RIS) Supporting Info

**摘要** 以聚乙二醇和共嵌段化合物 F127 为双模板剂, 采用溶胶-凝胶辅助水热法制备了球形介孔  $\text{TiO}_2$  (MS- $\text{TiO}_2$ )。采用扫描电镜、透射电镜、X 射线衍射、热重分析和低温 N<sub>2</sub> 吸附-脱附对样品进行了结构表征, 并以苯酚为降解模型物在紫外光下对其活性进行了评价。结果表明, 所得  $\text{TiO}_2$  为球形介孔结构, 孔径为 6.5~12.6 nm, 比表面积最高可达 106.9 m<sup>2</sup>/g, 孔体积 0.21 cm<sup>3</sup>/g, 球形颗粒直径 200~300 nm, 由粒径为 15~20 nm 的小晶粒组成。随着焙烧温度的升高,  $\text{TiO}_2$  的比表面积和孔体积减小, 孔径增大。双模板剂的使用比单一模板剂更能形成稳定的立体网状球形胶束, 并有效抑制  $\text{TiO}_2$  前驱体的团聚, 诱导其形成球形介孔结构。其中, 在 500 oC 下焙烧所制 MS- $\text{TiO}_2$  样品表现最高的光催化活性, 苯酚降解率达 86.4%, 为  $\text{TiO}_2$  的 1.3 倍。

关键词: 双模板 二氧化钛 介孔 球形 表面活性剂 苯酚

**Abstract:** Mesoporous  $\text{TiO}_2$  (MS- $\text{TiO}_2$ ) spheres were prepared by a sol-gel assisted hydrothermal method using double-surfactant (PEG and F127) as templates. Scanning electron microscopy, transmission electron microscopy, X-ray diffraction, thermal gravimetry, and N<sub>2</sub> adsorption-desorption were used for catalyst structural characterization. Phenol was used as a model compound for photocatalytic activity test. The results showed that MS- $\text{TiO}_2$  spheres with uniform diameter of 200~300 nm, which was composed by 15~20 nm of  $\text{TiO}_2$  crystals, can be obtained. Maximum specific surface area as high as 106.9 m<sup>2</sup>/g, together with pore diameter of 6.5~12.6 nm and pore volume of 0.21 cm<sup>3</sup>/g can be achieved under the optimum conditions. With increasing calcination temperature, specific surface area and pore volume of MS- $\text{TiO}_2$  decreased, and pore diameter enlarged. Double templates can form a more stable spherical micelle, inhibit the growth and particle aggregation of  $\text{TiO}_2$  precursor and promote its self-assembly into spherical structure. MS- $\text{TiO}_2$  prepared at 500 °C exhibited the highest activity with the phenol degradation of 86.4%, which is about 1.3 times that of  $\text{TiO}_2$  without templates.

Keywords: double template, titanium dioxide, mesopore, sphere, surfactant, phenol

收稿日期: 2012-05-25; 出版日期: 2012-08-15

**Service**

- ▶ 把本文推荐给朋友
- ▶ 加入我的书架
- ▶ 加入引用管理器
- ▶ Email Alert
- ▶ RSS

**作者相关文章**

- ▶ 王殿平
- ▶ 刘守新

**引用本文:**王殿平, 刘守新 .溶胶-凝胶辅助水热双模板法制备球形介孔  $\text{TiO}_2$ [J] 催化学报, 2012,V33(10): 1681-1688WANG Dian-Ping, LIU Shou-Xin .Preparation of Mesoporous  $\text{TiO}_2$  Spheres via Sol-Gel Assisted Hydrothermal Method Using Double Templates[J] Chinese Journal of Catalysis, 2012,V33(10): 1681-1688**链接本文:**<http://www.chxb.cn/CN/10.3724/SP.J.1088.2012.20532> 或 <http://www.chxb.cn/CN/Y2012/V33/I10/1681>

- [1] Yang H X, Qian J F, Chen Zh X, Ai X P, Cao Y L. *J Phys Chem C*, 2007, 111: 14067
- [2] 唐王朝, 黄显怀, 俞汉青, 胡春. 化学进展 (Tang Y Ch, Huang X H, Yu H Q, Hu Ch. *Chem Progr*), 2007, 19: 225
- [3] He Z L, Zhu Zh F, Li J Q, Zhou J Q, Wei N. *J Hazard Mater*, 2011, 190: 133
- [4] 王晓静, 刘超, 胡中华, 刘亚菲, 陈玉娟, 温祖标. 催化学报 (Wang X J, Liu Ch, Hu Zh H, Liu Y F, Chen Y J, Wen Z B. *Chin J Catal*), 2008, 29: 391
- [5] Varghese O K, Paulose M, Grimes C A. *Nat Nanotechnol*, 2009, 4: 592
- [6] Choi S Y, Mamak M, Coombs N, Chopra N, Ozin G A. *Adv Funct Mater*, 2004, 14: 335
- [7] Dong A G, Ren N, Tang Y, Wang Y J, Zhang Y H, Hua W M, Gao Z. *J Am Chem Soc*, 2003, 125: 4976
- [8] 向全军, 余家国. 催化学报 (Xiang Q J, Yu J G. *Chin J Catal*), 2011, 32: 525
- [9] 丁玉兰, 柏扬, 李伟, 陈闪山, 朱育丹, 朱银华, 杨祝红, 陆小华. 催化学报 (Ding Y L, Bai Y, Li W, Chen Sh Sh, Zhu Y D, Zhu Y H, Yang Zh H, Lu X H. *Chin J Catal*), 2010, 31: 1271
- [10] Serrano D P, Calleja G, Sanz R, Pizarro P. *Chem Commun*, 2004: 1000

- [11] Peng T Y, Zhao D, Dai K, Shi W, Hirao K. *J Phys Chem B*, 2005, 109: 4947
- [12] Yu J C, Yu J G, Zhang L Zh, Ho W. *J Photochem Photo-biol A*, 2002, 148: 263
- [13] Zhang Sh Q, Wen W, Jiang D L, Zhao H J, John R, Wilson G J, Will G D. *J Photochem Photobiol A*, 2006, 179: 305
- [14] Yoshitake H, Sugihara T, Tatsumi T. *Chem Mater*, 2002, 14: 1023
- [15] 李伟, 赵莹, 刘守新. 催化学报 (Li W, Zhao Y, Liu Sh X. *Chin J Catal*), 2012, 33: 342
- [16] Jing X Zh, Li Y X, Yang Q B, Yin Q R. *Mater Sci Eng B*, 2004, 110: 18
- [17] Antonelli D M, Ying J Y. *Angew Chem, Int Ed*, 1995, 34: 2014
- [18] Yang P D, Zhao D Y, Margolese D I, Chmelka B F, Stucky G D. *Nature*, 1998, 396: 152
- [19] Yusuf M M, Imai H, Hirashima H. *J Sol-Gel Sci Technol*, 2003, 28: 97
- [20] 王晓静, 刘超, 胡中华, 刘亚菲, 陈玉娟, 温祖标. 催化学报 (Wang X J, Liu Ch, Hu Zh H, Liu Y F, Chen Y J, Wen Z B. *Chin J Catal*), 2008, 29: 391
- [21] Chen D H, Huang F Zh, Cheng Y B, Caruso R A. *Adv Mater*, 2009, 21: 2206
- [22] Sheng Q R, Cong Y, Yuan Sh, Zhang J L, Anpo M. *Micro-porous Mesoporous Mater*, 2006, 95: 220
- [23] Smatt J H, Schunk S, Linden M. *Chem Mater*, 2003, 15: 2354
- [24] Zhao J Q, Wan P, Xiang J, Tong T, Dong L, Gao Zh N, Shen X Y, Tong H. *Micro-porous Mesoporous Mater*, 2011, 138: 200
- [25] Zhang X T, Zhou G W, Xu J, Bai G W, Wang L. *J Solid State Chem*, 2010, 183: 1394
- [26] Kim D S, Ham S J, Kwak S Y. *J Colloid Interf Sci*, 2007, 316: 85
- [27] 刘守新, 陈孝云, 陈曦. 催化学报 (Liu Sh X, Chen X Y, Chen X. *Chin J Catal*), 2006, 27: 697
- [28] Hüsing N, Launay B, Doshi D, Kickelbick G. *Chem Mater*, 2002, 14: 2429
- [29] Torma V, Peterlik H, Bauer U, Rupp W, Hüsing N, Bernstorff S, Steinhart M, Goerigk G, Schubert U. *Chem Mater*, 2005, 17: 3146
- [30] Shrinivasan S, Breadmore M C, Hosticka B, Landers J P, Norris P M. *J Non-Cryst Solids*, 2004, 350: 391
- [31] 刘茜, 李宏旭, 钱斌, 高焕新, 王仰东, 唐颐, 谢在库. 催化学报 (Liu Y, Li H X, Qian B, Gao H X, Wang Y D, Tang Y, Xie Z K. *Chin J Catal*), 2008, 29: 733
- [32] 张雅心, 张学军. 北京化工大学学报 (Zhang Y X, Zhang X J. *J Beijing Univ Chem Technol*), 2010, 37(5): 83
- [33] Yang J, Ferreira J M F. *Mater Lett*, 1998, 36: 320
- [34] Yu J G, Wang G H, Cheng B, Zhou M H. *Appl Catal B*, 2007, 69: 171
- [35] Parida K M, Naik B. *J Colloid Interf Sci*, 2009, 333: 269
- [36] Guo W, Luo G S, Wang Y J. *J Colloid Interf Sci*, 2004, 271: 400
- [37] Alberius P C A, Frindell K L, Hayward R C, Kramer E J, Stucky G D, Chmelka B F. *Chem Mater*, 2002, 14: 3284
- [38] Yoo K S, Lee T G, Kim J. *Micro-porous Mesoporous Mater*, 2005, 84: 211
- [39] Shamaila S, Sajjad A K L, Chen F, Zhang J L. *Catal Today*, 2011, 175: 568
- [40] Bu Sh J, Jin Zh G, Liu X X, Yang L R, Cheng Zh J. *Mater Chem Phys*, 2004, 88: 273
- [41] Yu J C, Zhang L Zh, Yu J G. *New J Chem*, 2002, 26: 416
- [42] Ding X J, An T Ch, Li G Y, Zhang Sh Q, Chen J X, Yuan J M, Zhao H J, Chen H, Sheng G Y, Fu J M. *J Colloid Interf Sci*, 2008, 320: 501
- [43] Blin J L, Leonard A, Yuan Zh Y, Gigot L, Vantomme A, Cheetham A K, Su B L. *Angew Chem, Int Ed*, 2003, 42: 2872
- [1] 唐苏苏, 胡臻, 余定华, 邹彬, 江凌. 功能化离子液体修饰的 SBA-15 固定化 *Burkholderia cepacia* 脂肪酶[J]. 催化学报, 2012, 33(9): 1565-1571
- [2] 司维峰, 李换巧, 尹杰, 李书双, 谢妍, 李佳, 吕洋, 刘元, 邢永恒, 徐缓, 宋玉江. 球形分枝结构 Pt 纳米催化剂的合成、纯化及电催化性能[J]. 催化学报, 2012, 33(9): 1601-1607
- [3] 洪伟, 刘百军, 陈玉.  $TiO_2-Al_2O_3$  的水热法合成及其负载的 NiMoP 催化剂上 FCC 柴油加氢脱硫性能[J]. 催化学报, 2012, 33(9): 1586-1593
- [4] 马璇璇, 朱银华, 李力成, 王昌松, 陆小华, 杨祝红. 介孔  $TiO_2$  晶须担载 Au 的热稳定性[J]. 催化学报, 2012, 33(9): 1480-1485
- [5] 刘龙杰, 张艳华, 王爱琴, 张涛. 介孔氧化钨担载 Pt 催化剂上甘油氢解制备 1,3-丙二醇[J]. 催化学报, 2012, 33(8): 1257-1261
- [6] 李艳荣, 宋明娟, 顾海芳, 黄曜, 牛国兴, 赵东元. 适合 SBA-15 介孔材料工业化生产的改良方法[J]. 催化学报, 2012, 33(8): 1360-1366
- [7] 丛燕青, 李哲, 张轶, 王齐, 徐谦, 伏芳霞.  $Fe_2O_3/TiO_2$  纳米管的制备及其光电催化降解染料废水性能[J]. 催化学报, 2012, 33(8): 1402-1409
- [8] 廖兰, 黄彩霞, 陈劲松, 吴月婷, 韩志钟, 潘海波, 沈水发. 高比表面积 CuPc/ $TiO_2$  纳米管复合材料的制备及其可见光光催化活性[J]. 催化学报, 2012, 33(6): 1048-1054
- [9] 陈孝云, 陆东芳, 林淑芳. S 掺杂  $S-TiO_2/SiO_2$  可见光响应光催化剂的制备及性能[J]. 催化学报, 2012, 33(6): 993-999
- [10] 刘成, 谭蓉, 孙文庆, 银董红. 离子液体功能化有序介孔 SBA-15 孔壁定域磷钨酸催化活性中心构建及其催化性能研究[J]. 催化学报, 2012, 33(6): 1032-1040
- [11] 张波, 汤明慧, 袁剑, 吴磊. 负载型  $ZrO_2$  催化苯甲醛 Meerwein-Ponndorf-Verley 反应中的载体效应[J]. 催化学报, 2012, 33(6): 914-922
- [12] 赵慧敏, 苏芳, 范新飞, 于洪涛, 吴丹, 全燮. 石墨烯-二氧化钛复合催化剂对光催化性能的提高[J]. 催化学报, 2012, 33(5): 777-782

- [13] 周强, 范宝玲, 许东兴, 付明来. CdS/TiO<sub>2</sub> 纳米管可见光催化剂的制备、表征及光催化活性[J]. 催化学报, 2012, 33(5): 850-856
- [14] 王卫, 陆春华, 苏明星, 倪亚茹, 许仲梓. N 掺杂富含 (001) 晶面 TiO<sub>2</sub> 纳米片的制备及 N 掺杂浓度对可见光催化活性的影响[J]. 催化学报, 2012, 33(4): 629-636
- [15] 党高飞, 石艳, 付志峰, 杨万泰. 磁性 Fe<sub>3</sub>O<sub>4</sub>@PS@PAMAM-Ag 复合催化粒子的制备及其可再生催化性能[J]. 催化学报, 2012, 33(4): 651-658