非水溶剂热法制备 (001) 面暴露的 F/TiO₂ 纳米晶及其光催化活性

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摘要: 采用非水体系溶剂热法制备了 (001) 面暴露的锐钛矿相 F/TiO₂ 纳米光催化剂. 结果表明, F 的掺杂对 TiO₂ 纳米单晶的形成影响很大. 一方面, F 离子作为晶面导向剂稳定 (001) 晶面, 形成 (001) 面暴露的锐钛矿相 TiO₂; 另一方面, F 离子也起到稳定剂作用, 抑制纳米粒子的快速生长. 以光催化降解甲基橙为模型反应比较了不同 F/TiO₂ 样品和商业 P25 样品的光催化活性. 同时, 通过选用不同捕获剂, 研究了 F/TiO₂ 和 P25 样品在甲基橙降解反应中的活性物种.

关键词: 氟掺杂; 二氧化钛; 光催化; (001) 晶面; 甲基橙

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Synthesis and Photocatalytic Activity of F/TiO₂ Nanocrystals with Exposed (001) Facets via a Nonhydrolytic Solvothermal Route

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Abstract: F/TiO₂ nanocrystals with exposed (001) facets were synthesized by a nonhydrolytic solvothermal route. The influence of F ions on the formation process was investigated in detail. The F ions function as a crystal-face directing agent and a stabilizing agent. The photocatalytic activities of the F/TiO₂ and commercial P25 samples were determined by the degradation of methyl orange. The influencing factors and active species in the degradation process are discussed after particular characterization and experiments with different scavengers.

Key words: fluorine doping; titania; photocatalysis; (001) facet; methyl orange

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TiO₂ 纳米晶因具有独特的光电效应而备受关注, 已成为最具应用前景的光催化剂之一^[1~3]. 在通常情况下, 锐钛矿 TiO₂(101) 面表面能因低于 (001) 面而更容易暴露, 很难得到其他面暴露的锐钛矿 TiO₂. 这限制了对不同晶面, 尤其是 (001) 高能面性质的研究^[4~7]. 最近, Yang 等^[4]合成了 (001) 面暴露率

为 47% 的微米级单晶锐钛矿 TiO₂, 为进一步深入研究 (001) 面的物化性质提供了可能. 相比于微米级晶体, 纳米晶更适合作为表面化学与实际技术沟通的桥梁. Han 等^[5]首次报道了 (001) 面暴露率高达 89% 的锐钛矿相 TiO₂ 纳米单晶, 在光催化降解甲基橙 (MO) 反应中, (001) 面暴露的纳米单晶片光催化活性

比(101)面暴露的锐钛矿相更高. 随后, Dai等^[6]合成了十面双锥状(001)面暴露率为9.6%的锐钛矿TiO₂. Liu等^[7]利用水热法制备了(001)面暴露率为18%的纳米级锐钛矿相TiO₂. 但在上述工作中, 大都使用HF以得到纳米级(001)面暴露的TiO₂. 而直接使用HF较危险且会造成严重的环境污染.

另一方面, 材料表面和结构与其性能间的关系已成为材料和催化领域的研究热点^[8,9]. 目前, (001)面暴露的TiO₂纳米晶已应用于光催化降解污染物、光催化制氢和染料敏化太阳能电池等领域^[10~15]. 最近, 我们采用非水体系醇热法制备了具有高比表面积(106 m²/g)和高(001)面暴露率43%的规则十面体锐钛矿相纳米TiO₂单晶^[16]. 但到目前为止, 在非水醇热法的制备过程中, F离子对纳米单晶的影响尚未被深入研究. 因此本文通过控制前驱体中F/Ti的摩尔比, 讨论了TiO₂纳米晶体的生长和(001)面的形成及其光催化活性, 并提出了表面F修饰的(001)面暴露TiO₂纳米颗粒与商业P25不同的降解机理.

1 实验部分

1.1 催化剂的制备

在磁力搅拌下, 于40℃将0.07 ml的TiCl₄缓慢滴入40 ml叔丁醇中配成溶液. 再在搅拌条件下, 加入不同浓度的NH₄F溶液, 以控制混合溶液中的F和Ti的摩尔比($R_{F/Ti}$)分别为0, 0.5, 1, 2和4. 混合液搅拌1 h后转移到水热釜中, 保持水热釜的填充度在80%, 密封后于160℃保持2 d, 生成大量白色沉淀. 将白色沉淀离心分离, 并依次用二次蒸馏水和无水乙醇洗涤, 在80℃干燥12 h. 制得的样品标记为F/TiO₂-x (x为 $R_{F/Ti}$). 作为对比用的样品为Degussa公司的商业P25.

1.2 催化剂的表征

采用Rigaku Dmax-3C型多晶X射线衍射(XRD)仪(Cu K_α靶, $\lambda = 0.15418$ nm)测定样品晶相. 使用日本电子公司JEM2010型透射电子显微镜(TEM)观察催化剂的颗粒尺寸和结晶形态. 用MC-2530紫外可见分光光度计(UV-Vis)测定样品的光吸收. 使用NOVO 4000型气体吸附分析仪在液氮温度(-196℃)下测定N₂的吸附-脱附等温线, 并得到催化剂的比表面积. 样品的表面元素电子态由X射线光电子能谱(XPS, Perkin-Elmer PHI 5000)获得, 并

根据F 1s和Ti 2p峰面积计算表面F/Ti摩尔比, 校正用的C 1s碳谱电子结合能(BE)为284.8 eV. 样品的荧光光谱(PL)在Varian Cary-Eclipse 500型荧光光谱仪上获得.

1.3 催化剂的评价

在100 ml的圆柱形石英反应器中评价催化剂的光催化活性. 取0.050 g催化剂于50 ml初始浓度为20 mg/L的甲基橙溶液中. 以4个功率为8 W, 特征波长为365 nm的紫外灯管作为光源, 光源与石英反应器的距离为10 cm, 预吸附1 h达到吸附平衡后进行降解测试, 控制反应温度为30℃, 搅拌速率为800 r/min. 光照降解1 h后取上层清液, 用UV 7504/PC型紫外-可见分光光度计在464 nm处测得吸光度, 并由此计算出MO降解率. 空白试验显示, 在有光照而无催化剂时, MO降解率不到5%, 因此可基本忽略其对催化活性的影响. 每次活性测试均重复三次以上, 重复实验结果在允许的误差范围以内($\pm 2.5\%$).

2 结果与讨论

2.1 F/TiO₂样品的晶相结构和性质

图1是不同F/Ti摩尔比F/TiO₂样品的XRD谱. 可以看出, 各样品在 $2\theta = 25.3^\circ$, 37.8° 和 48.0° 处出现锐钛矿相TiO₂(101), (004)和(200)晶面衍射峰(JCPDS 21-1272), 表明样品具有很好的锐钛矿晶相^[17]. 随着 $R_{F/Ti}$ 的增加, 样品衍射峰逐渐增强, 表明在TiO₂体系中F的引入使得锐钛矿相结晶度增加. Yu等^[18]也发现类似现象. 另外, 当不加F时, 所得样

图1 不同F/Ti摩尔比F/TiO₂样品的XRD谱

Fig. 1. XRD patterns of F/TiO₂ samples with different F/Ti molar ratios. (1) 0; (2) 0.5; (3) 1; (4) 2; (5) 4.

品在 $2\theta = 27.5^\circ$ 处出现一个微弱的金红石相衍射峰. 而 F 的加入使得该峰消失, 表明 F 的修饰有利于抑制金红石相的生成. 可见, 所制样品均为纯锐钛矿相. 同时, F 的加入并未使 TiO_2 样品的 (101) 面衍射峰发生明显偏移, 说明 F 没有进入 TiO_2 晶格中. 表 1 为通过 Scherrer 公式算得所制样品的平均晶粒尺寸. 由表可见, 当 $R_{\text{F/Ti}} \leq 3$ 时, 样品晶粒尺寸缓慢从 12 nm 增加到 18 nm; 而当 $R_{\text{F/Ti}} = 4$ 时, 晶粒尺寸迅速增至 42 nm.

由图还可以看出, 样品 (004) 晶面衍射峰明显宽于 (101), 表明 F/TiO₂-1 样品可能沿着特定的轴向生

表 1 不同 F/TiO₂ 样品的结构参数
Table 1 Structural parameters of different F/TiO₂ samples

$R_{\text{F/Ti}}$	$R_{\text{F/Ti}}^{\text{a}}$ (%)	A_{BET} (m ² /g)	Crystal size ^b (nm)	Percentage of (001) facets (%)	A_{BET} of (001) facets (m ² /g)
0	0	132	11	8	11
0.5	8	165	12	16	26
1	10	136	15	36	49
2	11	102	18	40	41
4	14	60	42	—	—
P25	0	50	23	—	—

^a $R_{\text{F/Ti}}$ is the F/Ti ratio on the surface and calculated by XPS spectra (F 1s and Ti 2p). ^bCrystal size of anatase.

长. 我们通过计算 (101), (200) 和 (004) 方向得到的晶粒尺寸可估算出纳米单晶 TiO_2 (001) 面的暴露率^[16]. 所得结果见表 1. 由表可见, 样品 (001) 面的暴露率随着 F 掺杂量的增加而逐渐增加. 当 $R_{\text{F/Ti}} = 2$ 时, 暴露率可达 40%. 由于 $R_{\text{F/Ti}} = 4$ 样品形貌很不均匀, 因而未估算其 (001) 面暴露率.

图 2 为不同 $R_{\text{F/Ti}}$ 比 F/TiO₂ 样品的 TEM 照片. 由图可见, 不加 F 时, 只能获得团聚的纳米颗粒; $R_{\text{F/Ti}}$ 增加到 0.5 时, 团聚的样品逐渐分散; 至 $R_{\text{F/Ti}} = 1$ 时, 可制得单分散的纳米颗粒且主要呈现正方形和六边形. 图 2(d) 是从 [001] 晶轴角度拍到的正方形颗粒的 HRTEM 照片, 可观察到两个相互垂直的晶轴. 沿这两个晶轴方向测得的晶面间距均为 0.189 nm, 与文献报道的 (200) 面和 (020) 面的晶面间距一致^[19], 这进一步证明所合成的样品是暴露 (001) 面的锐钛矿纳米单晶. 在水热法中, 也观察到通过 HF 中的 F 诱导晶体定向生长的现象^[4,5]. 当 $R_{\text{F/Ti}}$ 增加到 2, F/TiO₂ 样品的纳米晶粒形貌变得更为清晰, 说明颗粒的结晶度有所增加, 同时其晶粒尺寸也逐渐增大, 与 XRD 结果一致. 当 $R_{\text{F/Ti}} = 4$ 时, 样品中存在大晶粒, 且晶体发生了一定程度的扭曲甚至变形, 晶粒尺寸大小及

图 2 不同 F/Ti 摩尔比 F/TiO₂ 样品的 TEM 照片

Fig. 2. TEM images of F/TiO₂ samples with different F/Ti molar ratios. (a) 0; (b) 0.5; (c) 1; (d) 1 (high resolution image); (e) 2; (f) 4.

形貌不再均一.

图3是不同F/Ti摩尔比F/TiO₂样品的XPS谱. 由图可见, 所有F/TiO₂样品中Ti物种都以Ti⁴⁺形式存在于TiO₂. 高浓度F掺杂TiO₂时出现的“阴影效应”^[20]未在本文出现. 然而, 随着 $R_{F/Ti}$ 的增加, O 1s在530.1和532.1 eV处有两个不同的信号峰, 分别对应于TiO₂中的晶格氧和表面吸附的•OH^[21,22]. 而在纯TiO₂样品中只在530.1 eV处出现信号峰. 可以看出, 随F浓度的增加, F/TiO₂样品于532.1 eV处的峰强度明显增加, 说明表面•OH组分逐渐增加. F物种通常

图3 不同F/Ti摩尔比F/TiO₂样品的XPS谱

Fig. 3. XPS spectra of F/TiO₂ samples with different F/Ti molar ratios. (1) 0; (2) 0.5; (3) 1; (4) 2; (5) 4.

以两种方式掺杂于TiO₂中^[4]: (1) 表面吸附的F物种 (BE = 684.1 eV), 主要以吸附态存在于TiO₂表面; (2) 取代晶格中的O原子形成Ti-F键 (BE = 688.5 eV). 本文所制的F/TiO₂样品只在684.4 eV出现峰, 说明F只吸附于单晶TiO₂的表面. 此外, 随着前驱溶液中F浓度的增加, F信号峰逐渐增强. 通过F 1s和Ti 2p的峰面积可算出表面的F/Ti摩尔比 ($R_{F/Ti}^s$, 见表1). 可以看出, $R_{F/Ti}^s$ 并没有随初始 $R_{F/Ti}$ 的增加而显著变化.

另外由表1可见, F/TiO₂-0.5样品的比表面积最高, 为165 m²/g, 且晶粒尺寸也较小. 但随着 $R_{F/Ti}$ 的增加, F/TiO₂样品的比表面积逐渐减小, 可能与晶粒尺寸的增加有关. 当 $R_{F/Ti}$ = 4时, 样品的比表面积降到60 m²/g. 虽然纯TiO₂样品的晶粒尺寸最小, 但其比表面积并非最大. 由图2可知, 纳米颗粒的团聚可能是导致其比表面积变小的原因之一.

由于在整个制备(001)晶面暴露的TiO₂纳米晶的过程中都没有使用HF. 因此这种方法是一种新的绿色环保路线. 同时, F的添加对TiO₂纳米晶的形成影响较大. 当不加F时, 由于没有物种可以稳定(001)晶面, 导致无法得到(001)面暴露的样品; 同时也无法稳定纳米粒子, 导致纳米晶之间的团聚. 随着F用量的增加 ($R_{F/Ti}$ = 1), 由于表面吸附F, 得到的纳米晶体也逐渐分散. 此外, (001)面的暴露率随 $R_{F/Ti}$ 的增加而逐渐增加. 当F浓度增加后, 更多的F以吸附态积聚在TiO₂表面, 使(001)面的表面能降低到低于(101)面, 导致晶体定向生长为(001)面暴露的TiO₂纳米晶. 因此, F离子具有两个作用: (1) 作为晶面导向剂, 诱导晶体沿(001)面定向生长; (2) 作为稳定剂以阻止小晶粒的团聚. 这主要与表面吸附的F使样品表面带负电有关, 由静电力产生的排斥力抑制了纳米颗粒的团聚.

2.2 F/TiO₂样品的UV-Vis和PL谱

图4为不同样品的UV-Vis谱. 纯TiO₂样品禁带宽度为3.2 eV, 因而在可见光下无响应. 引入F后, 样品在可见光区仍没有明显响应, 表明表面吸附F对TiO₂禁带宽度没有影响. 但随着 $R_{F/Ti}$ 从0.5增加至1, 样品在紫外光区的吸收明显增强; 至 $R_{F/Ti}$ = 4时, 样品光吸收反而有所下降. 可见, F/TiO₂-1样品的紫外吸收最强. 实际上, 紫外吸收受比表面积、表面组成和晶体结构等多种因素的影响. 由于F/TiO₂-1样品

图 4 不同 F/Ti 摩尔比 F/TiO₂ 样品的 UV-Vis 谱

Fig. 4. UV-Vis DRS spectra of F/TiO₂ samples with different F/Ti molar ratios. (1) 0; (2) 0.5; (3) 1; (4) 2; (5) 4.

比表面积仅次于 F/TiO₂-0.5. 因此 F/TiO₂-0.5 的紫外吸收明显高于 F/TiO₂-0, F/TiO₂-2 和 F/TiO₂-4. 但 F/TiO₂-1 的紫外吸收却高于 F/TiO₂-0.5. 仔细比较后发现, 这两个样品的表面组成也接近. 但 F/TiO₂-1 中 (001) 面的暴露率为 36%, 而 F/TiO₂-0.5 仅为 16%. 因此可以认为, 二者不同的本征晶体结构, 尤其是其 (001) 面的暴露率可能是造成样品紫外吸收不同的原因之一.

我们进一步用荧光光谱研究了光生载流子捕获、移动和迁移的效率. 荧光光谱的发射峰由自由载流子的复合产生, 可反映电子-空穴对在半导体材料中的复合几率^[23]. 图 5 为不同 F/Ti 摩尔比 F/TiO₂ 样

图 5 不同 F/Ti 摩尔比 F/TiO₂ 样品的荧光光谱

Fig. 5. PL spectra of F/TiO₂ samples with different F/Ti molar ratios. The wavelength of exciting light is 280 nm (500 eV). (1) 0; (2) 0.5; (3) 1; (4) 2; (5) 4.

品的 PL 谱. 由图可见, 与其他 F/TiO₂ 相比, F/TiO₂-1 的荧光峰强度较弱, 表明光生电子-空穴对的复合速率较低. 但该样品具有较大的比表面积和较高的 (001) 面暴露率, 表明其表面层有更多的 (001) 面暴露, 这与 (001) 面的比表面积相关 (见表 1). 综上所述, (001) 面比表面积与荧光峰的变化趋势相反, 即 (001) 面比表面积越高, 荧光发射峰越弱, 光生电子-空穴对的复合率也越低.

2.3 F/TiO₂ 样品的光催化活性

以光催化降解甲基橙为模型反应, 研究了 F/TiO₂ 系列样品的光催化活性, 结果见图 6. 由图可见, 随着 $R_{F/Ti}$ 由 0 增加至 1, F/TiO₂ 的光催化活性逐渐增加. $R_{F/Ti}$ 继续增加时, 样品活性反而下降. 可见, F/TiO₂-1 样品光催化活性最高. 一般地, 光催化活性受催化剂晶相、结晶度、比表面积和元素掺杂等多种因素影响^[24~28]. 为了考察 F 对样品光催化活性的影响, 本文依次用 NaOH 和 HCl 溶液处理 F/TiO₂-1 样品以除去 F, 结果发现处理后样品活性降至 43%, 可见 F 的存在对样品光催化活性有所促进. 对于其他 F/TiO₂ 样品表面 F 和 TiO₂ 的摩尔比变化不大. 因此, 样品活性不仅仅取决于表面吸附的 F 离子. 另外, 样品比表面积差异也很难解释 F/TiO₂-1 光催化活性最高. 但由前文可以看出, F/TiO₂-1 样品的 (001) 面比表面积最大. 由此可见, 样品活性与其 (001) 晶面的比表面积成线性关系. 这与 UV-Vis 和 PL 结果一致. 另外, F/TiO₂-1 的活性是商业 P25 的两倍, 可见

图 6 不同 F/Ti 摩尔比 F/TiO₂ 样品及商业 P25 的光催化活性

Fig. 6. Photocatalytic activity of F/TiO₂ samples with different F/Ti molar ratios. (1) 0; (2) 0.5; (3) 1; (4) 2; (5) 4; (6) P25.

F/TiO₂-1 具有潜在的应用价值.

采用不同中间体捕获剂可进一步研究降解物/催化剂反应体系的主要活性物种. 为了明确 F/TiO₂ 和 P25 光催化降解 MO 的反应路径, 本文检测了反应过程中的 $\cdot\text{OH}$ 、 $\cdot\text{O}_2^-$ (超氧自由基) 和空穴. 一般来说, 异丙醇作为 $\cdot\text{OH}$ 的淬灭剂^[29-31], 甲醇作为空穴的淬灭剂^[30,31], 而对苯醌则是 $\cdot\text{O}_2^-$ 的淬灭剂^[32]. 事实上, $\cdot\text{OH}$ 可以通过电子传递过程或者光生空穴反应形成, 而 $\cdot\text{O}_2^-$ 只能通过电子的传递获得. 相应实验结果见图 7. 由图可见, 在 MO/F/TiO₂ 体系中, 所有的 $\cdot\text{OH}$ 、 $\cdot\text{O}_2^-$ 和空穴对于最终的活性都有贡献, 其贡献大小顺序为: 空穴 < $\cdot\text{OH}$ < $\cdot\text{O}_2^-$. 但是对于 MO/P25 体系, 只有捕获 $\cdot\text{O}_2^-$ 才能抑制 MO 的光催化降解. 由此可见, MO/P25 体系中, MO 直接和 $\cdot\text{O}_2^-$ 作用; 而对于 MO/F/TiO₂ 体系, 所有的空穴、 $\cdot\text{OH}$ 和 $\cdot\text{O}_2^-$ 都起到活性物种的作用.

图 7 F/TiO₂-1 和商业 P25 样品加入不同牺牲剂后的光催化活性

Fig. 7. Photocatalytic activity of F/TiO₂-1 (a) and P25 (b) samples by addition of different scavengers. (1) No scavenger; (2) 100 mmol/L isopropyl alcohol; (3) 100 mmol/L methyl alcohol; (4) 1 mmol/L benzoquinone.

3 结论

采用非水溶剂热法制备了不同(001)面暴露率的锐钛矿相 F/TiO₂ 纳米晶光催化剂. F 的加入对

F/TiO₂ 纳米晶的形成起到晶面导向剂和稳定剂的作用. 催化剂(001)晶面的比表面积对提高其在紫外光区的吸收和降低光生电子-空穴对的复合起促进作用. 在系列 F/TiO₂ 催化剂中, 以(001)晶面比表面积最高的 F/TiO₂-1 样品的光催化活性最高, 且明显优于商业 P25 样品. 在光催化降解 MO 过程中, 在 F/TiO₂ 上所有的空穴、 $\cdot\text{OH}$ 和 $\cdot\text{O}_2^-$ 都可能起到活性物种的作用, 而在 P25 催化剂上只有 $\cdot\text{O}_2^-$ 一种活性物种起作用.

参 考 文 献

- 1 Fujishima A, Honda K. *Nature*, 1972, **238**: 37
- 2 Li H, Bian Z, Zhu J, Huo Y, Li H, Lu Y. *J Am Chem Soc*, 2007, **129**: 4538
- 3 Snaith H J, Schmidt-Mende L. *Adv Mater*, 2007, **19**: 3187
- 4 Yang H G, Sun C H, Qiao S Z, Zou J, Liu G, Smith S C, Cheng H M, Lu G Q. *Nature*, 2008, **453**: 638
- 5 Han X G, Kuang Q, Jin M S, Xie Z X, Zheng L S. *J Am Chem Soc*, 2009, **131**: 3152
- 6 Dai Y Q, Cobley C M, Zeng J, Sun Y M, Xia Y N. *Nano Lett*, 2009, **9**: 2455
- 7 Liu G, Sun C H, Yang H G, Smith S C, Wang L Z, Lu G Q, Cheng H M. *Chem Commun*, 2010, **46**: 755
- 8 Liu S W, Yu J G, Jaroniec M. *J Am Chem Soc*, 2010, **132**: 11914
- 9 Xiang Q J, Lv K L, Yu J G. *Appl Catal B*, 2010, **96**: 557
- 10 Amano F, Prieto-Mahaney O O, Terada Y, Yasumoto T, Shibayama T, Ohtani B. *Chem Mater*, 2009, **21**: 2601
- 11 Zhang D Q, Li G S, Wang H B, Chan K M, Yu J C. *Cryst Growth Des*, 2010, **10**: 1130
- 12 Yu J G, Xiang Q J, Ran J R, Mann S. *CrystEngComm*, 2010, **12**: 872
- 13 Alivov Y, Fan Z Y. *J Phys Chem C*, 2009, **113**: 12954
- 14 Yu J G, Qi L F, Jaroniec M. *J Phys Chem C*, 2010, **114**: 13118
- 15 Yu J G, Fan J J, Lv K L. *Nanoscale*, 2010, **2**: 2144
- 16 Zhu J, Wang S H, Bian Z F, Xie S H, Cai C L, Wang J G, Yang H G, Li H X. *CrystEngComm*, 2010, **12**: 2219
- 17 Alberius P C A, Frindell K L, Hayward R C, Kramer E J, Stucky G D, Chmelka B F. *Chem Mater*, 2002, **14**: 3284
- 18 Yu J G, Liu S W, Yu H G. *J Catal*, 2007, **249**: 59
- 19 Jun Y W, Casula M F, Sim J H, Kim S Y, Cheon J, Alivisatos A P. *J Am Chem Soc*, 2003, **125**: 15981
- 20 Liu H M, Yang W S, Ma Y, Cao Y, Yao J N, Zhang J, Hu T D. *Langmuir*, 2003, **19**: 3001
- 21 Kurtz R L, Stockbauer R, Madey T E, Roman E, Desegovia J L. *Surf Sci*, 1989, **218**: 178
- 22 Gopel W, Anderson J A, Frankel D, Jaehnig M, Phillips K, Schafer J A, Rocker G. *Surf Sci*, 1984, **139**: 333
- 23 Jing L Q, Qu Y C, Wang B Q, Li S D, Jiang B J, Yang L B, Fu W, Fu H G, Sun J Z. *Sol Energ Mat Sol C*, 2006, **90**: 1773
- 24 Zhu J, Bian Z F, Ren J, Liu Y M, Cao Y, Li H X, Dai W L,

- He H Y, Fan K N. *Catal Commun*, 2007, **8**: 971
- 25 Huo Y N, Zhang X Y, Jin Y, Zhu J, Li H X. *Appl Catal B*, 2008, **83**: 78
- 26 Yu J C, Li G S, Wang X C, Hu X L, Leung C W, Zhang Z D. *Chem Commun*, 2006: 2717
- 27 Zhang D Q, Li G S, Wang F, Yu J C. *CrystEngComm*, 2010, **12**: 1759
- 28 Li G S, Zhang D Q, Yu J C. *Phys Chem Chem Phys*, 2009, **11**: 3775
- 29 Minero C, Mariella G, Maurino V, Vione D, Pelizzetti E. *Langmuir*, 2000, **16**: 8964
- 30 Cheng S P, Zhu Y F. *Environ Sci Technol*, 2010, **44**: 5570
- 31 Zhuang J D, Dai W X, Tian Q F, Li Z H, Xie L Y, Wang J X, Liu P, Shi X C, Wang D H. *Langmuir*, 2010, **26**: 9686
- 32 Palominos R, Freer J, Mondacab M A, Mansilla H D. *J Photochem Photobiol A*, 2008, **193**: 139

英 译 文

English Text

As one of the most promising photocatalysts, TiO_2 nanocrystals have received plenty of attention recently because of their special photovoltaic performance [1–3]. In most cases TiO_2 nanocrystals with an anatase crystal structure have surfaces with (101) facets because of their lower surface energy compared with that of (001) facets, and this has limited further investigation into the property of (001) facets [4–7]. Recently, Yang et al. [4] reported the synthesis of micron-sized anatase single crystals with dominant (001) facets (47%), which provides a new method to investigate the physical and chemical properties of (001) facets. To bridge the gap between surface chemistry and technical applications, a nanosized crystal is more suitable than a micron-sized crystal. Nanosized anatase TiO_2 with a high percentage of exposed (001) facets (89%) was first reported by Han et al. [5]. In the photocatalytic degradation of methyl orange (MO), the nanosheets showed high activity indicating the superior activity of the anatase (001) facets. More recently, Dai et al. [6] synthesized a truncated tetragonal bipyramidal-shaped crystal with 9.6% of the surface enclosed by (001) facets. Liu et al. [7] reported the hydrothermal synthesis of nanosized anatase TiO_2 single crystals with 18% (001) facets. However, in most cases HF is essential for the synthesis of nanosized anatase crystals with exposed (001) facets. The direct use of HF is dangerous and environmentally detrimental.

On the other hand, much effort has been devoted to investigations into the surface and structure-dependent properties in the material and catalysis research field [8,9]. Many studies about TiO_2 nanosheets with exposed (001) facets have recently been reported for different applications such as photocatalysis, H_2 -production, and solar cells [10–15]. Re-

cently, we reported a new nonhydrolytic solvothermal method to synthesize regular decahedron nanocrystals with a large surface area of about $106 \text{ m}^2/\text{g}$ and the crystals contained a high percentage of exposed (001) facets of about 43% on average [16]. However, the influence of F in the nonhydrolytic solvothermal method has not been investigated to date. In this work, the F/Ti was controlled to evaluate the growth of crystals and the formation of exposed (001) facets. Moreover, this work provides new insights into and an understanding of the increase in photocatalytic activity of the surface-fluorinated anatase single crystal. Different degradation mechanisms for the surface-fluorinated TiO_2 nanocrystals and the pure TiO_2 sample are proposed.

1 Experimental

1.1 Preparation

Typically, 0.07 ml of titanium chloride (TiCl_4) was slowly added to 40 ml of *tert*-butanol (TBA) under vigorous stirring at 40°C , and this was designated solution A. The solution B was composed of a certain amount of NH_4F . The solution B was then transferred to the solution A under vigorous stirring over 1 h. The nominal molar ratios of fluorine to titanium ($R_{\text{F/Ti}}$) were 0, 0.5, 1, 2, and 4. The mixed solution was then transferred to a 50 ml Teflon-lined autoclave until 80% of its volume was reached. The autoclave was sealed and maintained at 160°C for 2 d. White precipitates were collected, washed with distilled water, rinsed in ethanol, and then dried in an oven at 80°C overnight. The obtained samples were marked F/ TiO_2 - x (x being the F/Ti molar ratios). Pure TiO_2 (P25, from Degussa) was also used for comparison.

1.2 Characterization

X-ray diffraction (XRD) patterns were collected to confirm the composition on a Rigaku Dmax-3C with $\text{Cu } K_\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$). The size and morphology of the powders were determined using a JEM-2010 transmission electron microscope (TEM). UV-Vis diffuse reflectance spectra (UV-Vis DRS) were collected on a MC-2530 instrument. N_2 adsorption-desorption isotherms were determined by the BET method on a NOVA 4000 at -196°C . The surface area (A_{BET}) was calculated using the BJH method. The surface electronic states were analyzed by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5000) and the surface F/Ti molar ratio was determined based on the area ratio of the principal XPS peaks for the F 1s and Ti 2p levels. All the binding energies were referenced to the C 1s peak at 284.8 eV. Light absorption was detected using photoluminescence (PL) spectra (Varian Cary-Eclipse 500).

1.3 Photocatalytic activity test

The photocatalytic reaction was carried out at 30 °C in a 100 ml quartz reactor containing 0.050 g catalyst and 50 ml of 20 mg/L MO as an aqueous solution at pH = 6–7. The reaction system was stirred vigorously (800 r/min) to eliminate the diffusion effect on the reaction kinetics. The mixture was allowed to stir for > 1 h to reach the adsorption equilibrium. The photocatalytic reaction was then initiated by irradiating with four 8 W UV lamp (365 nm) located around the solution at a distance of 10 cm. Each reaction lasted for 1 h and the MO concentration was analyzed by UV spectrophotometry (Xinmao UV-7504PC) at its characteristic wavelength ($\lambda = 464$ nm). Preliminary tests showed that there was a good linear relationship between light absorbance and the concentration of the organic compounds. Experimental results also confirmed that less than 5% of the MO was decomposed after a 1 h reaction in the absence of the photocatalyst and thus, could be neglected in comparison with the degradation yield resulting from real photocatalysis. The reproducibility of the results was determined by repeating the experiments at least three times and was found to be within acceptable limits ($\pm 2.5\%$).

2 Results and discussion

2.1 Structure analysis of the F/TiO₂ samples

Figure 1 shows XRD patterns of the F/TiO₂ samples with different F/Ti molar ratios. The results show that all the F/TiO₂ samples are comprised of a well crystallized anatase phase corresponding to the characteristic diffraction peaks around 2θ values of 25.3° (101), 37.8° (004) and 48.0° (200) [17]. With an increase in $R_{\text{F/Ti}}$, the peak intensities increase in strength indicating an increase in anatase crystallinity by the introduction of F into TiO₂. A similar result was reported by Yu et al. [18] who found that fluoride increases the crystallinity of anatase. In fact, a small diffraction peak at $2\theta = 27.5^\circ$ is attributed to the rutile phase and it has been observed in a F/TiO₂-0 sample. In other F doped F/TiO₂ samples this peak has been found to disappear, which indicates that doping with F can restrain the growth of the rutile phase. No other significant diffraction peaks were observed in the other F/TiO₂ samples implying that a pure anatase phase was obtained. In addition, no obvious shift of the principle (101) peak of TiO₂ occurred after F-doping suggesting that the F species was not incorporated into the TiO₂ lattice. Using the Scherrer equation, the crystal size was also calculated and is shown in Table 1. At a $R_{\text{F/Ti}} \leq 3$, the crystal size gradually increased from 12 to 18 nm. At a $R_{\text{F/Ti}} = 4$, the crystal size quickly increased to 42 nm.

A detailed analysis of the XRD pattern reveals that the

intensities of the (004) diffractions are obviously broader than that of the (101) diffractions, which may imply that oriented growth of the F/TiO₂-1 sample occurs along the special axis. According to the method proposed by our group in a previous paper [16] the percentage of exposed (001) facets can be estimated by calculating the crystal size from the (101), (200), and (004) orientations. The results are listed in Table 1. It seems that the percentage of exposed (001) facets gradually increases with an increase in F content. At $R_{\text{F/Ti}} = 2$, this percentage reaches 40%. The percentage of exposed (001) facets for F/TiO₂-4 was not estimated because of its inhomogeneous morphology, as discussed in the following TEM analysis.

The influence of $R_{\text{F/Ti}}$ on the sample's morphology was examined by TEM. Figure 2 shows that the F content has an important role during the formation of F/TiO₂ nanocrystals. Without F, only the aggregated nanocrystals were obtained. By increasing the F content to $R_{\text{F/Ti}} = 0.5$, the aggregated nanocrystals disperse. At $R_{\text{F/Ti}} = 1$, dispersed nanocrystals are obtained. In Fig. 2(c), these nanocrystals are mainly dispersed as squares or hexagons. Figure 2(d) shows a HRTEM image of a square-shaped crystal. Two perpendicular square plane lattices were observed. Along both directions each lattice d -spacing is about 0.189 nm, which corresponds to the (200) or (020) facets of anatase TiO₂ [19] and this further confirms the presence of a single crystalline anatase structure with exposed (001) facets. A similar oriented growth that was induced by F has also been observed when using the hydrothermal method [4,5]. With a further increase in $R_{\text{F/Ti}}$ to 2, the shape of the nanocrystals is clearer, which implies an increase in crystallinity. The observed crystal size of F/TiO₂-2 increased compared to that of F/TiO₂ with a low F content. These results are consistent with the XRD analysis. For $R_{\text{F/Ti}} = 4$, a very large crystal was observed. It seems that the obtained crystal is distorted to some extent and the distribution of crystal sizes is nonuniform.

XPS spectra were used to investigate the surface properties. Figure 3 shows the Ti 2p, O 1s, and F 1s core level XPS spectra of the F/TiO₂ samples with various $R_{\text{F/Ti}}$. The evolution of the Ti 2p signal indicates that the Ti species in all the F/TiO₂ samples can be attributed to the Ti⁴⁺ of TiO₂. The "shadowing effect" [20], which is often observed in high content carbon doped TiO₂ samples was not found in our samples. However, an obvious difference was found in the O 1s and F 1s core level XPS spectra (Fig. 3(b) and (c)). With an increase in $R_{\text{F/Ti}}$, the O 1s signal has two contributions at 530.1 and 532.1 eV. In the pure TiO₂ sample, only one peak was observed at 530.1 eV. The main peak at ca. 530.1 eV can be attributed to the lattice oxygen in TiO₂ while the signal at ca. 532.1 eV is associated with surface hydroxyl groups [21,22]. The peaks at ca. 532.1 eV increased obviously with an increase in F content, indicating an increase in the surface

hydroxyl groups. More information about the F species was obtained from the F 1s signal (Fig. 3(c)). In the literature, generally two types of F are observed in the TiO₂ samples [4]. One is a surface adsorbed F species from the exchange between F and surface hydroxyl groups located at ca. 684.1 eV. The other is a lattice replacement of O, which results in a Ti–F band located at ca. 688.5 eV. All the F/TiO₂ samples give one peak at 684.4 eV, which reveals that only the adsorbed F ion is present. With an increase in the F concentration of the precursor solution, the F 1s signal gradually increases. The real molar ratio of F and Ti ($R_{\text{F/Ti}}^{\text{s}}$) was calculated from an integral of the two peaks that correspond to F 1s and Ti 2p. The results are shown in Table 1. It is interesting to find that $R_{\text{F/Ti}}^{\text{s}}$ did not change greatly with an increase in $R_{\text{F/Ti}}$.

The specific surface area (A_{BET}) was measured and the results are summarized in Table 1. The highest A_{BET} of about 165 m²/g was obtained for F/TiO₂-0.5, which has a small crystal size. Upon an increase in $R_{\text{F/Ti}}$, the A_{BET} gradually decreases because of a further increase in the crystal size. For F/TiO₂-4, the A_{BET} reaches 60 m²/g. The pure TiO₂ sample with the smallest crystal size did not give the largest A_{BET} . Intensive aggregation may be a possible reason and this was confirmed by TEM analysis.

For the full synthesis no HF was used, which provides a green route for the preparation of TiO₂ nanocrystals with exposed (001) facets. The added F ions play important roles. When $R_{\text{F/Ti}} = 0$, no species stabilize the (001) crystal faces and only aggregated mixed crystals are obtained. With an increase in the F content ($R_{\text{F/Ti}} = 1$), the crystals dispersed homogeneously. On the other hand, the percentage of exposed (001) facets also increased by varying $R_{\text{F/Ti}}$. By increasing the F content, more F ions are adsorbed and gradually accumulate on the surfaces of TiO₂ until the surface free energy of the (001) surface is below that of the (101) surface. This results in the formation of TiO₂ nanocrystals with exposed (001) facets and, therefore, two functions of the F ion are proposed. One is a crystal-face directing agent that induces the oriented growth to expose the high energy (001) facets. Another is a stabilizing agent that protects against the aggregation of small nanocrystals. Because of the surface adsorbed F, the repulsive force was increased to disperse the nanocrystals.

2.2 UV-Vis DRS and PL analysis of the F/TiO₂ samples

The UV-Vis DRS spectra (Fig. 4) show that the pure TiO₂ samples are inactive in the visible range because of the large energy bandgap (3.2 eV). By inducing F no obvious response is observed in the visible region. This reveals that the surface adsorbed F has no influence on the bandgap of TiO₂. A significant difference was found in the UV region. With an

increase in $R_{\text{F/Ti}}$ from 0.5 to 1, the absorption of UV light increased. By further increasing the $R_{\text{F/Ti}}$ to 4, light absorbance did not increase but decreased. F/TiO₂-1 had the highest UV absorbance.

The UV absorbance of the F/TiO₂ nanocrystals may be influenced by many factors such as surface area, surface components as well as crystallinity. By comparison with the other samples, the surface area of F/TiO₂-1 was less than that of F/TiO₂-0.5. Therefore, the UV absorbance of F/TiO₂-1 is larger than that of F/TiO₂-0, F/TiO₂-2, and F/TiO₂-4. However, it is difficult to understand why the UV absorbance of F/TiO₂-1 is larger than that of F/TiO₂-0.5. Considering that the F content of F/TiO₂-1 (10%) is similar to that of F/TiO₂-0.5 (8%) the difference may be related to the intrinsic crystal structure. The percentage of exposed (001) facets in F/TiO₂-1 sample is about 36%, while in F/TiO₂-0.5 it is about 16%. The obvious different percentages of exposed (001) facets may be one of the reasons that determine the UV absorbance.

Further PL spectra were also examined to investigate the efficiency of charge carrier trapping, migration, and transfer (Fig. 5). The PL emission results from the recombination of free carriers and can reflect the fate of electron-hole pairs in semiconductor particles [23]. As shown in Fig. 5, F/TiO₂-1 had a much weaker PL peak than the other F/TiO₂ samples suggesting a lower recombination rate between photoelectrons and holes. By comparison with the other samples, F/TiO₂-1 has a larger surface area as well as a higher percentage of exposed (001) facets. This means that F/TiO₂-1 has more exposed surfaces of the (001) crystal face near the surface layer, which is the real A_{BET} of the (001) facets ($A_{\text{BET}(001)}}$). The $A_{\text{BET}(001)}}$ of all the samples was calculated in Table 1. This shows that the $A_{\text{BET}(001)}}$ and PLS intensity trends are opposite to each other, which means that a higher $A_{\text{BET}(001)}}$ will result in a lower PLS intensity as well as a lower recombination rate between photoelectrons and holes.

2.3 Photocatalytic activities of the F/TiO₂ samples

The photocatalytic degradation of MO was chosen as a model reaction to evaluate the photocatalytic activities of the studied F/TiO₂ samples (Fig. 6). Upon an increase in $R_{\text{F/Ti}}$ from 0 to 1, the activity of F/TiO₂ increased gradually. However, a further increase in the $R_{\text{F/Ti}}$ to 2 or 4 caused a decrease in activity. F/TiO₂-1 had the highest photocatalytic activity. In general, the photocatalytic activity is influenced by many factors such as crystal phase, crystallinity, surface area, and doped ions [24–28]. To illustrate the role of F, pure TiO₂ with exposed (001) facets were prepared by washing F/TiO₂-1 with a NaOH solution followed by a HCl solution. We found that only 43% degradation was obtained without the modification of F. This result demonstrates that modifi-

cation by F promotes photocatalytic activity. In the other F/TiO₂ samples, the real F^s/TiO₂ did not change much and, therefore, such a great change in activity was not mainly influenced by the surface adsorbed F ions. With an increase in crystal size, the surface area gradually decreased. By only considering the change in surface area, it is difficult to explain the highest activity obtained for F/TiO₂-1. Taking into account the change in the percentage of exposed (001) facets, we found that the $A_{\text{BET}(001)}$ of F/TiO₂-1 was the largest. The $A_{\text{BET}(001)}$ value correlates with the increase in activity. These results indicate that the $A_{\text{BET}(001)}$ of the (001) facets may play an important role in determining the final activity, which is consistent with the result from UV-DRS and PL spectra. For comparison, the activity of P25 was also evaluated. We found that the activity of F/TiO₂-1 is about two times higher than that of P25, indicating a potential application for F/TiO₂-1.

The reaction process was also investigated to determine the primary active species in the MO/catalyst system. To determine the paths involved in the photocatalytic degradation of MO over the F/TiO₂ and P25 samples, we analyzed for •OH and •O₂⁻ using radical and hole scavengers. In general isopropyl alcohol acts as a •OH scavenger [29–31] and methanol acts as a hole scavenger [30,31]. The tests were carried out as follows: (1) no scavenger, (2) 100 mmol/L isopropyl alcohol, (3) 100 mmol/L methyl alcohol, (4) 1 mmol/L benzoquinone. Benzoquinone acts as a •O₂⁻ scavenger [32] and in fact, •OH can form by electron-transfer

mediation or a photogenerated holes reaction. •O₂⁻ can only be obtained by electron-transfer mediation. The results are shown in Fig. 7 and in the MO/F/TiO₂ system, all the •OH and •O₂⁻ radicals and holes contribute to the final activity according to the following order: holes < •OH < •O₂⁻. For the MO/P25 system, only •O₂⁻ suppresses the degradation of MO. In the MO/P25 system MO reacts directly with •O₂⁻. In the MO/F/TiO₂ system, for all the holes, •OH and •O₂⁻ are the active species.

3 Conclusions

Different F/TiO₂ samples with exposed (001) facets were synthesized by a facile nonhydrolytic solvothermal method. The results show that the initially added F ions play two roles in the formation of TiO₂ nanocrystals with exposed (001) facets. One is as a crystal-face direct agent and the other is as a stabilizing agent. The surface area of the (001) facets is most important for the increased absorbance of UV light as well as a lower recombination rate between the photoelectrons and holes. F/TiO₂-1 has the highest photocatalytic activity and it is superior to commercial P25. For the degradation of MO all the holes, •OH and •O₂⁻ may act as an active species on F/TiO₂. Only one active species (•O₂⁻) was produced on P25.

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