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Communication (Dedicated to Professor Yi Chen on the occasion of his 80th birthday)

Fluoride-free synthesis of anatase TiO₂ crystals rich in (001) facets in the presence of cationic polymer

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ABSTRACT

Controllable syntheses of anatase TiO₂ rich in (001) facets have attracted much attention because of the excellent photocatalytic activity of this material in dye degradation. These syntheses are normally performed in the presence of fluoride, which is environmentally unfriendly. In this study, anatase TiO₂ crystals rich in (001) facets were successfully synthesized in the presence of a cationic polymer and characterized using X-ray diffraction, scanning electron and transmission electron microscopies, and ultraviolet-visible spectroscopy. Photocatalytic tests showed that this material is very active in the degradation of methyl orange compared with conventional anatase TiO₂ crystals and a commercial P25 photocatalyst. The high activity is attributed to the rich (001) facets translation.

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Anatase TiO₂ crystals have been extensively studied because of their wide range of applications in photocatalysis [1], solar energy conversion [2], photonic devices [3], and sensors [4]. Generally, the (001) facets of anatase TiO₂ crystals are considered to be very active in photocatalysis [5]. However, it is very difficult to synthesize anatase TiO₂ crystals rich in (001) facets because of the high surface energy. The most exposed surface of anatase TiO₂ crystals is the thermodynamically stable (101) facet, which can account for more than 94% of the total crystal surface in conventional anatase TiO₂ crystals [6]. There is therefore great interest in the development of controllable syntheses of anatase TiO₂ crystals rich in (001) facets.

Since a breakthrough in synthesizing anatase TiO₂ crystals with a large percentage of (001) facets in the presence of fluoride species was made [7], much effort has been devoted to developing new routes for preparing anatase TiO₂ crystals rich

in (001) facets in the presence of fluoride species [8–13]. For example, Alivov et al. [8] reported transformation of TiO₂ nanotubes to pyramid-shaped TiO₂ nanoparticles with a high percentage of (001) facets in the presence of fluoride species, and Han et al. [13] successfully synthesized TiO₂ nanosheets with a high percentage of exposed (001) facets in the presence of a highly concentrated HF solution. Despite much encouraging progress in recent years, the synthesis of anatase TiO₂ crystals rich in (001) facets still requires the presence of fluoride species; these are highly toxic and corrosive in the gas or liquid state. It is therefore highly desirable to develop a new synthetic strategy for the fluoride-free synthesis of anatase TiO₂ crystals rich in (001) facets.

In this paper, we report a new fluoride-free synthesis of anatase TiO₂ crystals rich in (001) facets in the presence of a cationic polymer (poly(diallyldimethylammonium chloride),

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PDDA-Cl). Interestingly, the obtained material is very active in the photocatalytic degradation of methyl orange (MO) compared with conventional anatase TiO_2 crystals and the commercial P25 photocatalyst.

In a typical synthesis of anatase TiO_2 crystals rich in (001) facets, 4 mmol of titanium tetrabutoxide (Aladin) were added dropwise to 30 mL of ethanol. After stirring for 4 h, 1.5 g of PDDA-Cl were added. Then the mixture was continuously stirred overnight at room temperature and transferred to a Teflon-lined stainless-steel autoclave. After crystallization at 160 °C for 4 d, the products were separated by centrifugation, washed with deionized water, and dried at 100 °C for 1 h. After calcination at 550 °C, anatase TiO_2 crystals rich in (001) facets were finally obtained; this was designated TiO_2 -P.

Figure 1(a) shows X-ray diffraction (XRD) patterns of samples synthesized in the presence or absence of PDDA-Cl. Both samples have peaks indexed to anatase TiO_2 crystals (JCPDS No. 21-1272). Interestingly, the ultraviolet-visible (UV-Vis) diffuse reflectance spectrum of TiO_2 -P synthesized in the presence of PDDA-Cl shows stronger absorption in both the UV and visible regions than those of TiO_2 crystals synthesized in the absence of PDDA-Cl (Fig. 1(b)). This is in good agreement with previously reported results [14–16] and is attributed to differences among the sample morphologies.

Figure 2 shows scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of various TiO_2 samples. The SEM images of the TiO_2 -P sample show well-defined rectangular crystals with side lengths of about 1.2–1.5 μm and thicknesses of about 0.5 μm . According to the symmetry of anatase TiO_2 crystals, for a single truncated pyramid in each anatase TiO_2 crystal, the top flat and square surface should be (001) facets, and the isosceles trapezoidal surfaces should be (101) facets. Figure 2(c) shows a high-magnification

Fig. 1. XRD patterns (a) and UV-Vis spectra (b) of TiO_2 crystals synthesized in the absence (1) and presence (2) of PDDA-Cl.

TEM image of TiO_2 -P viewed from the top (the inset is the fast Fourier transform (FFT) pattern); the observed sets of lattices oriented perpendicular to each other with an equal fringe spacing of 0.19 nm are in good agreement with the (200) and (020) planes of anatase TiO_2 [17,18]. This image shows a typical top view of (001) facets on anatase TiO_2 . Based on the above

Fig. 2. SEM (a, b) and TEM (c) images of TiO_2 -P sample (inset is the corresponding FFT pattern of (c)); SEM (d) and TEM (e, f) images of TiO_2 sample synthesized in the absence of PDDA-Cl.

Fig. 3. (a) Photocatalytic properties of various TiO₂ samples in MO degradation under UV irradiation (MO, $C_0 = 10$ mg/L). (1) Blank; (2) TiO₂ synthesized in the absence of PDDA-Cl; (3) P25; (4) TiO₂-P. (b) Recyclability of the TiO₂-P sample.

structural information, the percentage of highly active (001) facets in the TiO₂-P sample was estimated to be as high as 72%. In contrast, the TiO₂ sample synthesized in the absence of PDDA-Cl is mainly composed of spherical crystals of diameter 3–5 μm (Fig. 2(d)). The TEM image of the sample shows a lattice spacing of about 0.35 nm, which is consistent with that of the (101) facets (Fig. 2(f)).

The degradation of MO was chosen as a model to determine the photocatalytic activity of the TiO₂-P sample; commercially available P25 (average particle size 25 nm) was used as a reference for comparison. The photocatalytic activity of the TiO₂-P sample is much higher than that of TiO₂ synthesized in the absence of PDDA-Cl, and even higher than that of the commercial P25 catalyst, as shown in Fig. 3(a). The anatase phase is the same (Fig. 1(a)) and the surface areas are similar for the TiO₂-P (48 m²/g) and conventional TiO₂ (38 m²/g), so the much higher activity of TiO₂-P than that of conventional TiO₂ is attributed to the much larger number of exposed (001) facets in the TiO₂-P crystals. The TiO₂ crystals rich in (001) facets are very active for MO degradation compared with conventional TiO₂. It is also worth mentioning that the TiO₂-P sample had very good recyclability. When the sample was recycled four times, the sample activity was still comparable with that of the fresh catalyst (Fig. 3(b)).

The role of PDDA-Cl in the synthesis of TiO₂ crystals rich in (001) facets can be explained by interactions of surface Ti species with PDDA-Cl as a result of electrostatic coulombic forces, giving Ti⁴⁺-Cl⁻-PDDA⁺. Similar interactions have been widely observed in the assembly of cationic surfactants, chlorides, and inorganic cations in the synthesis of mesoporous materials [19–21]. Because the amount of exposed Ti on the (001) surface is twice that on the (101) surface, PDDA-Cl species are more likely to be adsorbed on the (001) surface, leading to suppression of growth in the (001) crystal direction [22]. As a result, the TiO₂-P sample is rich in photocatalytically active (001) facets.

In summary, we successfully synthesized anatase TiO₂-P crystals rich in (001) facets in the presence of PDDA-Cl under F-free conditions. The activity of the TiO₂-P in MO degradation

is much higher than those of conventional TiO₂ crystals and a commercial P25 catalyst. The controllable synthesis of oxides with preferred crystal facets using PDDA-Cl is potentially important for the future design and preparation of functional oxide materials.

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Graphical Abstract

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Fluoride-free synthesis of anatase TiO₂ crystals rich in (001) facets in the presence of cationic polymerWeiwei Chang, Yan Liu, Qi Sun, Xiangju Meng*, Feng-Shou Xiao*
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Anatase TiO₂ crystals rich in (001) facets were successfully synthesized in the presence of a cationic polymer under fluoride-free conditions. The crystals had high photocatalytic activity and good recyclability.

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具有丰富(001)面的锐钛矿TiO₂晶体的无氟合成常伟伟, 刘 艳, 孙 琦, 孟祥举*, 肖丰收[#]

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摘要: 采用一种全新的方法实现了无氟、在阳离子聚合物参与下合成具有丰富(001)面的锐钛矿TiO₂晶体(TiO₂-P), 并通过X射线衍射、扫描电镜、透射电镜、紫外-可见光谱等手段对样品进行了表征。光催化测试显示, 该样品对甲基橙的降解具有比常规锐钛矿TiO₂和商业P25更好的活性, 这可归因于TiO₂-P具有大量的暴露(001)晶面。

关键词: 锐钛矿二氧化钛; (001)晶面; 溶剂热合成; 阳离子聚合物; 高光催化活性

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锐钛矿TiO₂晶体广泛应用于光催化^[1]、太阳能转换^[2]、光子器件^[3]以及传感器^[4]等领域, 因而得到了广泛研究。通常, 该晶体的(001)晶面被认为具有很高的光催化活性, 但是该晶面的比表面能较高, 在晶体成核和生长的过程中很难合成出暴露大量(001)晶面的锐钛矿TiO₂晶体^[5]。对于普通的锐钛矿TiO₂, 暴露最多的是热力学稳定的(101)晶面, 通常可以占据整个晶体表面的94%以上^[6]。因此, 人们强烈期望控制合成出暴露大量高活性(001)晶面的锐钛矿TiO₂晶体。

自从Yang等^[7]在F⁻参与的条件首次合成出具有丰富(001)晶面的锐钛矿TiO₂晶体以来, 人们投入大量的精力发展了该路线^[8–13]。例如, Alivov等^[8]在NH₄F存在

下实现了从纳米管TiO₂向具有大量暴露(001)晶面的截头棱锥状纳米TiO₂颗粒的转变; Han等^[13]在高浓度HF溶液中成功制备出(001)面暴露率高达89%的锐钛矿TiO₂纳米片。尽管近年来在合成具有(001)晶面的锐钛矿TiO₂晶体方面已经取得了非常大的进展, 但是这些方法大都需要氟的参与, 而这些气相或液相的含氟化合物都具有高毒性和高腐蚀性。因此, 发展一种新的无氟合成方法以获得(001)晶面主导的锐钛矿TiO₂晶体显得十分迫切。

本文在无氟、阳离子聚合物聚二烯丙基二甲基盐酸盐(PDDA-Cl)参与的条件, 合成出了具有丰富(001)晶面的锐钛矿TiO₂晶体(TiO₂-P)。该样品在光催化降解甲

基橙反应中显示出比常规锐钛矿 TiO_2 晶体和商业P25更高的活性。

TiO_2 -P的合成过程如下。将4 mmol钛酸四丁酯(阿拉丁)缓慢滴加到30 mL无水乙醇中, 搅拌4 h, 然后滴加1.5 g PDDA-Cl, 于室温下搅拌过夜, 装入45 mL内衬为聚四氟乙烯的反应釜内; 将反应釜密闭并置于烘箱中, 于160 °C晶化4 d。取出后冷却至室温, 水洗并离心分离, 于100 °C干燥1 h, 550 °C焙烧5 h, 即得到具有丰富(001)晶面的锐钛矿 TiO_2 晶体。

图1(a)为所合成样品的X射线衍射(XRD)谱。可以看出, 在加入或不加入PDDA-Cl的情况下, 合成的样品均为纯的锐钛矿 TiO_2 晶体, 其主要衍射峰均与标准卡片(JCPDS 21-1272)相吻合。图1(b)为所合成样品的紫外-可见光谱。由图可见, 在PDDA-Cl存在下所合成的 TiO_2 -P样品在紫外光区和可见光区的吸收都明显强于未加PDDA-Cl时的, 这显然与样品的不同形貌有关, 类似现象的报道很多^[14-16]。

图2为不同 TiO_2 样品的扫描电镜(SEM)和透射电镜(TEM)照片。如图2(a)和(b)所示, TiO_2 -P样品由边长1.2–1.5 μm , 厚度约0.5 μm 的四面体晶体组成。依据锐钛矿 TiO_2 晶体的对称性, 在每个 TiO_2 晶体的截头棱锥面上, 上下顶部的四方平面为(001)晶面, 侧边的等腰梯形面为(101)晶面。图2(c)为高分辨TEM的顶部平面俯视图, 显示出该 TiO_2 -P样品顶部平面由互相垂直的晶格组成, 这些晶格的晶格间距约为0.19 nm, 这与锐钛矿 TiO_2 晶体的(200)和(020)平面相互垂直的情况吻合(图2(c)内插图), 进一步证实顶部的面为锐钛矿 TiO_2 的(001)晶面^[17,18]。根据以上形貌和结构信息可估算出合成的 TiO_2 -P样品所暴露的高活性(001)晶面约占72%。另一方面, 未加

PDDA-Cl条件下合成的 TiO_2 样品主要由直径约3–5 μm 的球状晶体组成(图2(d))。TEM结果(图2(f))显示其晶格间距约为0.35 nm, 对应于(101)晶面。

将甲基橙降解的反应作为模型反应来评价 TiO_2 -P样品的光催化活性, 并与商业P25 (平均粒径约为25 nm)进行比较, 结果见图3(a)。可以看出, 加入PDDA-Cl时所合成 TiO_2 -P样品的光催化活性比不加入PDDA-Cl时所合成样品的高得多, 甚至高于商业P25催化剂的。由于 TiO_2 -P样品和常规的 TiO_2 样品都是锐钛矿相(图1(a)), 并且它们具有可比较的比表面积, 因此两者光催化活性的不同可归因于其不同的晶面暴露状态。 TiO_2 -P样品与常规的 TiO_2 相比具有大量可暴露的高活性(001)晶面, 因此具有更高的光催化活性。值得一提的是, 该 TiO_2 -P样品循环使用4次, 其光催化活性仍然很高(图3(b)), 表现出很好的重复使用性能。

PDDA-Cl所起的作用可能与阳离子聚合物PDDA-Cl与表面钛物种的静电库仑作用力有关(Ti^{4+} - Cl^- -PDDA⁺)。这种作用力已被成功用于合成多种新结构与新组成的介孔材料^[19-21]。由于在(001)面暴露的Ti原子数目大约是(101)面的2倍, 因此PDDA-Cl更倾向于吸附在(001)表面, 从而抑制了晶体沿(001)方向上的过快生长^[22], 最终获得了具有大量暴露的高活性(001)晶面的 TiO_2 -P样品。

综上所述, 以阳离子聚合物PDDA-Cl为形貌控制剂, 在无氟条件下成功地合成出具有丰富(001)晶面的锐钛矿 TiO_2 晶体。与常规的锐钛矿 TiO_2 和商用P25催化剂相比, 该样品光催化降解甲基橙的活性更优异。这为利用PDDA-Cl来控制合成具有优势晶面的氧化物提供了新的思路与方法。