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Enhanced photocatalytic hydrogen generation of mesoporous rutile TiO₂ single crystal with wholly exposed {111} facets

Tingting Wu ^a, Xiangdong Kang ^a, Mohammad W. Kadi ^{b,#}, Iqbal Ismail ^b, Gang Liu ^{a,*}, Hui-Ming Cheng ^{a,b}

^aShenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, Liaoning, China

^bChemistry Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

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ABSTRACT

The development of semiconductor photocatalysts with highly reactive facets exposed has great potential to improve their photocatalytic reactivity. We report the synthesis of mesoporous rutile TiO₂ single crystals with tunable ratios of {110} and {111} facets through the seeded-template hydrothermal method. With increasing the amount of morphology controlling agent NaF, the facet ratio of {111} to {110} increases, and eventually the mesoporous rutile TiO₂ single crystals with wholly exposed {111} reactive facets are obtained. The resultant faceted mesoporous single crystals exhibit a superior photocatalytic performance of hydrogen evolution to mesoporous single crystals with a large percentage of thermodynamically stable {110} facets, as well as the solid rutile single crystals.

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1. Introduction

The development of semiconductor crystals with highly reactive facets has been one of the most effective strategies to improve their photocatalytic activity [1–7]. Since the pioneering work of synthesizing anatase TiO₂ single crystals with a high percentage of reactive {001} facets by Yang et al [8], in 2008, an unprecedented progress in the controllable synthesis of the faceted TiO₂ crystals has been achieved. So far, various modified strategies have been developed to prepare anatase TiO₂ crystals with different exposed facets, and the facet dependent photocatalytic properties have been well investigated [9–13]. Indeed, the selective exposure of specific reactive facets has been demonstrated to significantly improve the activity or

change the reaction preference of photocatalysts [14–15]. However, the single crystals with well-defined facets generally have a large particle size of several micrometers, which would lead to the prolonged bulk diffusion length of carriers, increased bulk recombination, and decreased surface area. In this sense, the development of porous single crystals with reactive facets exposed is expected to be an ideal solution to address these problems. Crossland et al. [16] developed a facile seeded template method to prepare mesoporous single crystal (MSC) anatase TiO₂ with well-developed facets, which delivered enhanced electron mobility and optoelectronic device performance relative to the conventionally used nanocrystalline TiO₂ film. This breakthrough opened up new opportunities of optimizing the performance of metal oxide semiconductors in var-

* Corresponding author. Tel: +86-24-23971088; Fax: +86-24-23971682; E-mail: gangliu@imr.ac.cn

Corresponding author. E-mail: mkadi@kau.edu.sa

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ious applications [17–19]. In comparison with anatase TiO_2 , rutile TiO_2 possesses additional advantages in photocatalysis applications such as overall water splitting [20]. However, there have only been several reports on the synthesis of porous rutile TiO_2 single crystals [18,21,22]. In particular, to the best of our knowledge, the controllable synthesis of mesoporous rutile TiO_2 with preferential {111} facets remains a challenge owing to the high surface energy of the {111} facets.

In this study, we synthesized mesoporous rutile TiO_2 single crystals with different ratios of {111}/{110} facets, and investigated the facet dependent activity in photocatalytic hydrogen evolution. The mesoporous single crystals were prepared through the seeded-template method by the hydrothermal treatment of TiCl_4 in the HCl solution containing NaF at 220 °C for 12 h. The corresponding control experiment without using a template was also performed to synthesize the solid single crystal (SSC), to enable the comparative study of both samples. NaF has been demonstrated to be an effective facet controlling agent in stabilizing the high energy facet {111} of rutile TiO_2 [23]. A series of mesoporous and solid rutile TiO_2 single crystals, with different exposed ratios of {110} and {111} facets, could be obtained by tuning the concentration of NaF. According to the different amount of NaF (20, 40, and 80 mg) added to Ti-containing precursor solution, these as-prepared samples were denoted as MSC-20, MSC-40, MSC-80 for mesoporous single crystals and SSC-20, SSC-40, SSC-80 for solid single crystals.

2. Experimental

2.1. Sample preparation

Seeded silica template was prepared based on the method given in the previous literature [16]. 50 nm silica spheres were synthesized by adding 32 mL H_2O , 18 mL ammonium hydroxide (30%) and 99 mL tetraethyl orthosilicate (TEOS, Sigma Aldrich) into 750 mL ethanol and stirred at 700 r/min for 24 h. The reaction solution was centrifuged at 5000 rpm for 5 h to form a quasi-close-packed bead template in a translucent solid. The unwashed solid was collected and sintered at 500 °C for 30 min. To seed the silica template, 25 g of the sintered template was immersed in 150 mL 15 mmol/L TiCl_4 solution, obtained by diluting a 2 mol/L TiCl_4 aqueous stock solution (the stock solution was prepared by diluting 100 mL TiCl_4 in 350 mL H_2O containing 1 mL 35 % HCl in an ice/water bath), and held at 70 °C for 1 h followed by thoroughly rinsing with deionized water. The dried template was resintered at 500 °C for 30 min.

Mesoporous rutile TiO_2 single crystal was prepared through a facile hydrothermal method [18,23]. The Ti-containing precursor solution was prepared by dropping 1.64 mL of 15 mmol/L TiCl_4 into 291 mL HCl solution under strong stirring in ice/water bath and further adding deionized water to 1 L. To prepare mesoporous rutile TiO_2 single crystal with different exposed {111} facets, 2 g of the seeded silica template was added to 40 mL of precursor solution containing 20, 40, and 80 mg NaF, respectively. The suspension was transferred to a Teflon-lined autoclave and heated at 220 °C for 12 h. The template

product was collected by centrifugation and fully washed with deionized water. To selectively etch the silica template, the sample was heated at 80 °C in a 2 mol/L NaOH solution for 1 h and then washed with deionized water and ethanol. In corresponding control experiment, solid rutile TiO_2 single crystal with different exposed {111} facets was prepared without template. The samples were heated at 600 °C for 2 h to remove surface-terminated F/Cl impurities.

2.2. Characterization

X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku diffractometer using $\text{Cu K}\alpha$ irradiation. Sample morphology and microstructure were characterized by scanning electron microscopy (SEM, Nova NanoSEM 430) and transmission electron microscopy (TEM, JEOL 2010). Brunauer-Emmett-Teller (BET) specific surface area was determined by nitrogen adsorption-desorption isotherm measurements at –196 °C (ASAP 2010). The optical absorbance spectra of the samples were recorded in a UV-visible spectrophotometer (JACSCO-550).

2.3. Photocatalytic hydrogen evolution measurement

Photocatalytic hydrogen evolution reactions were carried out in a top-irradiation vessel connected to a glass-enclosed gas circulation system. 100 mg of the single crystal TiO_2 powder was dispersed in 300 mL aqueous solution containing 10 vol% methanol. The deposition of 1 wt% Pt cocatalyst was conducted by directly dissolving H_2PtCl_6 in the above 300 mL reaction solution. The reaction temperature was maintained about 10 °C. Under irradiation of the 300 W Xe lamp, the amount of H_2 evolved was determined using gas chromatography (Agilent 6890).

3. Results and discussion

The amount of NaF dependent morphology evolution is shown in Fig. 1. It was clearly shown from the scanning electron microscopy (SEM) images that the porous samples exhibited a very similar morphology to that of the clearly faceted solid rutile TiO_2 single crystals, indicating the successful synthesis of porous single crystals with well-developed facets. According to the crystallographic symmetries of rutile TiO_2 , the four lateral rectangular facets in the middle part of the crystals are recognized as {110} facets and the eight triangular facets at the two ends of the crystals are {111} facets [12]. It was shown that the thermodynamically most stable rutile {110} facets disappeared gradually with increasing the amount of NaF, and eventually the rutile single crystals with wholly {111} facets were obtained when the amount of NaF was increased up to 80 mg. In contrast to the smooth facets in solid single crystals, many pores with a diameter of approximately 50 nm were observed after removing the silica beads, as expected. The type IV N_2 sorption isotherm curves and pore size distribution centered at about 50 nm confirmed the mesoporous structure (Fig. 2). It is worth noting that, although the morphology of the

Fig. 1. Low and high magnification SEM images for MSC-20 (a, d), MSC-40 (b, e) and MSC-80 (c, f) and high magnification SEM images for SSC-20 (g), SSC-40 (h) and SSC-80 (i).

mesoporous single crystals with different exposed facet ratios greatly changes, the specific surface area of these mesoporous samples are similar (24, 25, 28 m^2/g for MSC-20, MSC-40, MSC-80, respectively). In addition, mesoporous single crystals possess an average particle size of 300–500 nm, an order of magnitude smaller than that of solid single crystals ($\sim 3\text{--}5\ \mu\text{m}$). Apparently, this particle size difference could be attributed to the seeded nucleation and confinement of growth inside the mesoporous template. Note that several special single crystal particles, composed of a partial mesoporous and solid single crystal, were observed in all three mesoporous samples. This indicates the growth of single crystals from a seed located on or close to an external surface of the mesoporous template, which occurred inevitably in the synthesis of mesoporous single crystals using the seeded template method [16].

The microstructure of the mesoporous single crystals was

further investigated by transmission electron microscopy (TEM). Fig. 3 presents the distinct shapes of one crystal particle in the TEM images which clearly show the morphology transformation from the high aspect ratio of $\{110\}/\{111\}$ to the wholly $\{111\}$ facets. This is similar to the observed changes of solid single crystals (Fig. 1). Also, it reveals the uniformly distributed mesopores with a diameter of about 50 nm, consistent with the value of the pore distribution (Fig. 2), indicating the formation of a connected channel network throughout the whole framework. The corresponding selected area electron diffraction (SAED) patterns, in the insets of Fig. 3 recorded for the whole particle, show a set of sharp spots that are indexed to rutile TiO_2 , indicating the single crystal nature of the particle. The clear lattice fringes in the high resolution TEM images consistently suggest the high crystallinity of the mesoporous crystals.

Fig. 2. Nitrogen adsorption/desorption isotherms of mesoporous single crystal (MSC): (left) MSC-20, (middle) MSC-40 and (right) MSC-80, the pore size distributions of MSC are shown in the insets.

Fig. 3. TEM images of samples MSC-20(a), MSC-40(c) and MSC-80(e). High resolution TEM images of MSC-20(b), MSC-40(d) and MSC-80(f). The corresponding selected area electron diffraction (SAED) patterns are shown in the insets.

The phase identity and purity of the solid and mesoporous single crystal TiO_2 were investigated by X-ray diffraction (XRD). For solid single crystals, all the diffraction peaks of these three samples can be assigned to rutile TiO_2 and are very sharp, consistent with the solid particles comprising a single rutile crystal domain. The diffraction peaks of MSC-20 are identical to that of solid single crystal when 20 mg of NaF was added, as shown in Fig. 4. With increasing the amount of NaF to 40 and 80 mg, besides the dominant diffraction peaks of rutile TiO_2 , a very weak peak at 25.3° originating from the $\{01\}$ planes of anatase TiO_2 was detected. The presence of trace anatase phase could originate from the synergistic effect of the promoted nucleation of

Fig. 4. XRD patterns of samples MSC-20(1), MSC-40(2) and MSC-80(3). A: anatase; R: rutile.

the anatase phase and suppressed phase transformation from anatase to rutile by the high concentration of F^- ions [12]. Importantly, the diffraction peaks of all mesoporous rutile crystals are as sharp as those of the solid single crystals, in agreement with the porous particles being single crystal domains. This is also consistent with the TEM results. Overall, all these results suggest the synthesis of mesoporous rutile TiO_2 single crystals with tunable ratios of exposed facets.

Photocatalytic activities of these mesoporous and solid rutile TiO_2 single crystals were investigated by estimating the photocatalytic hydrogen generation from an aqueous solution containing methanol as a sacrificial agent. The light irradiation time was 5 h. Note that, prior to the test, all the samples were calcined in air at 600°C for 2 h to clean the surface without altering the morphology [16,18]. As shown in Fig. 5, the mesoporous rutile TiO_2 single crystals with wholly $\{111\}$ facets exhibited the highest hydrogen generation rate among the three mesoporous single crystal samples. As expected, the mesoporous single crystals with the most stable major $\{110\}$ facets gave the lowest hydrogen evolution rate, which was only half of that with wholly $\{111\}$ facets. The similar changing trend in photocatalytic activity was also observed in the solid single crystals. Evidently, these improvements could be dominantly attributed to the large exposure of reactive $\{111\}$ facets because they possessed the similar phase, microstructure, specific surface area and light absorption capability (Fig. 6(b)). However, the surface of these mesoporous crystals studied here were partially covered by fluorine species, which usually lowers the photocatalytic activity of TiO_2 by reducing the number of the unsaturated surface titanium atoms [4,11,12]. Although heating at around 600°C can effectively remove surface fluorine species from the samples, the collapse of the mesoporous structure is currently hard to avoid. It is anticipated that the photocatalytic activity of these mesoporous crystals can be greatly improved if a suitable method to remove surface fluorine without destroying mesoporous structure can be found. Notably, all mesoporous rutile single crystals show a much superior photocatalytic activity, by at least one order of magnitude, compared with their solid rutile single crystal counterparts. This

Fig. 5. Comparison of photocatalytic hydrogen generation after 5 h UV-visible irradiation over mesoporous and solid rutile TiO_2 single crystals with different percentages of exposed $\{111\}$ facets loaded with 1 wt% Pt in the presence of methanol as electron donor.

Fig. 6. UV-visible absorption spectra of solid single crystal rutile TiO₂ (a) and mesoporous single crystal rutile TiO₂ (b).

improvement could be related to the mesoporous structure features enabling an increased surface area for abundant surface active sites, shortened bulk diffusion length of carriers for the decreased bulk recombination and increased light absorbance from the connected mesoporous network, as indicated in Fig. 6.

4. Conclusions

In summary, mesoporous single crystal rutile TiO₂ with different exposed facets was synthesized through a seeded template method by changing the amount of NaF morphology controlling agent. The mesoporous single crystal rutile TiO₂ with wholly exposed {111} reactive facets exhibited a greatly enhanced photocatalytic activity relative to the mesoporous single crystals with a minority of {111} facets as well as the solid single crystals. This improvement is attributed to the synergistic effects of the increased surface reactive sites, long-range electron transport and light absorbance.

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Graphical Abstract

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Institute of Metal Research, Chinese Academy of Sciences, China; King Abdulaziz University, Saudi Arabia

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{111}晶面暴露对介孔金红石TiO₂单晶光催化产氢的促进作用

吴亭亭^a, 康向东^a, Mohammad W. Kadi^{b, #}, Iqbal Ismail^b, 刘岗^{a, *}, 成会明^{a, b}

^a中国科学院金属研究所沈阳材料科学国家(联合)实验室, 辽宁沈阳110016

^b阿普杜勒阿齐兹国王大学理学院化学系, 吉达21589, 沙特阿拉伯

摘要: 光催化反应发生在半导体材料的表面, 材料表面的原子/电子结构直接影响光催化剂的活性或选择性. 因此, 发展具有特定晶面的半导体光催化剂受到各国学者的普遍关注, 被认为是调控光催化材料性能的有效途径之一. 自2008年yang等首次合成高表面能{001}晶面占优的锐钛矿TiO₂单晶以来, 控制合成暴露不同晶面TiO₂晶体的研究得到了迅猛的发展, 已发展了多种方法合成了具有不同晶面的TiO₂晶体. 研究表明, 选择性地暴露特定的活性晶面能够显著地提高光催化剂的活性或者改变光催化反应的选择性. 但是, 含有完整晶面构型的TiO₂单晶样品的颗粒尺寸一般都较大, 通常为几微米, 因而显著增加了光生载流子传输与分离的难度, 并且导致材料较小的比表面积, 限制了对光催化活性的进一步提高. 能否在合成含特定晶面单晶的同时增加多孔结构成为有效解决这一问题的关键. 最近, Crossland等采用晶种模板法成功合成了介孔的锐钛矿TiO₂单晶, 并且通过光电器件研究证实了采用该思路可进一步提高材料的光电性能. 金红石TiO₂在光催化全分解水方面具有独特的优势, 然而关于多孔单晶金红石TiO₂的研究相对较少, 尤其是合成热力学不稳定的高表面能{111}晶面完全暴露的多孔金红石单晶面临较大的技术挑战因而一直未见文献报道.

本文利用晶种模板法, 以TiCl₄溶液为含Ti前驱体、NaF为形貌控制剂、采用水热处理制备出不同比例{111}晶面的介孔金红石单晶. 我们前期工作表明, NaF可作为形貌控制剂合成低表面能{110}晶面占优的介孔金红石单晶. 本文发现, 通过改变NaF的添加量, 可有效调变{111}/{110}晶面比例, 最终合成完全暴露{111}高表面能的介孔金红石TiO₂单晶. 扫描电镜结果显示, 当添加20 mg NaF时, 合成{110}占优的具有高长径比的介孔晶体; 当NaF用量增加到40 mg时{110}晶面进一步缩短; 至80 mg时则制备出{111}高能面完全暴露的金红石TiO₂晶体. 值得注意的是, 对比研究表明, 不采用模板合成了与多孔晶体完全相对应的不同{111}/{110}晶面比例的实心金红石晶体. 透射电镜及选区电子衍射以及结合X射线衍射进一步证实, 多孔的金红石TiO₂晶体与实心金红石单晶均都为单晶结构, 孔结构贯穿于样品内部且具有较高的晶面结晶性. 氮气吸附实验发现, 虽然三个不同晶面比例介孔金红石单晶样品间的形貌具有显著的差异, 但比表面积非常相近(分别为24, 25, 28 m²/g), 孔径也都为50 nm左右, 该值与所用SiO₂模板球的直径以及TEM观察结果相一致. 光催化产氢性能结果表明, 选择性的暴露活性晶面显著提高了光催化活性, 仅含高能面{111}的介孔金红石单晶样品具有最高的产氢速率(约800 μmol h⁻¹ g⁻¹), 比常规{110}晶面占优的介孔单晶样品速率提高了约一倍. 尤其比实心单晶样品的产氢速率提高了至少一个数量级, 这应归结于介孔结构特性所导致的表面反应活性位增加、电子传输距离缩短以及光吸收增强协同作用的结果.

关键词: 二氧化钛; 光催化剂; 介孔; 单晶; 产氢

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*通讯联系人. 电话: (024)23971088; 传真: (024)23971682; 电子信箱: gangliu@imr.ac.cn

[#]通讯联系人. 电子信箱: mkadi@kau.edu.sa

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