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Article (Special Issue on Environmental and Energy Catalysis)

Synthesis of TiO₂ mesocrystal film with enhanced photocatalytic activity

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ARTICLE INFO

Article history:

Received 30 November 2017

Accepted 13 December 2017

Published 5 April 2018

Keywords:

TiO₂ mesocrystals film

Photocatalysis

Hydrogen generation

Cr(VI) reduction

ABSTRACT

TiO₂ mesocrystals can considerably enhance charge separation owing to their oriented superstructures, with fewer internal defects and porous properties providing more active sites. In this work, we prepared TiO₂ mesocrystal films by a direct annealing method. The morphology and crystal phase of the film were controlled by adjusting the ratio of NH₄F and the calcination temperature. Moreover, we found that Au nanoparticles loaded on a TiO₂ mesocrystal film enabled highly efficient visible light photocatalytic properties. The photocatalytic activities were studied by hydrogen generation and photoreduction of Cr(VI). This work represents a considerable advance in the development and application of the TiO₂ mesocrystals.

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1. Introduction

Titanium dioxide (TiO₂) has been widely studied and applied in photocatalysis, solar energy conversion, and lithium-ion batteries owing to its ready availability, low cost, non-toxicity, and high stability [1–3]. In recent years, TiO₂ films have been widely studied, because of the difficulty of recovering powdered TiO₂ [4,5]. Hence, TiO₂ films are typically deposited on a substrate in the form of nanoparticles, to form polycrystalline and amorphous films [6,7]. Recently, films of TiO₂ nanotube arrays prepared by anodic oxidation technique have been widely used in photocatalysis, dye sensitized solar cells, and energy storage materials [8–10]. Single-crystalline anatase TiO₂ tetragonal nanosheet-array films have also been successfully prepared by hydrothermal methods [11]. The TiO₂ morphology and structure are among the most important aspects

that affect their light absorption, charge separation and transfer, reactant adsorption, and photocatalytic activity [12–15].

TiO₂ mesocrystals have recently emerged and received attention as a new class of porous TiO₂ materials with oriented superstructures of arranged TiO₂ nanocrystal building blocks [16–22]. Recent articles have focused on the preparation of TiO₂ materials with tailored framework structures through the addition of different templates and additives [23–29]. However, the preparation of mesoporous single crystal TiO₂ films has not yet been reported.

Modification of TiO₂ mesocrystals with Au nanoparticles also enables visible-light-driven photocatalytic performance. Au nanoparticles have a localized surface plasmon resonance (SPR), which can absorb light in the visible region owing to a resonant oscillation of free electrons [30].

Herein, we used a facile, direct annealing approach to fabri-

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This work was supported by the National Natural Science Foundation of China (21237003, 21407106, 21522703, 21377088), Shanghai Government (14ZR1430800, 13SG44, 15520711300), International Joint Laboratory on Resource Chemistry (IJLRC), and Ministry of Education of China (PCSIRT_JRT_16R49), the Program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning and Shuguang Research Program of Shanghai Education Committee.

DOI: 10.1016/S1872-2067(17)62980-2 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 39, No. 4, April 2018

cate a TiO_2 mesocrystal film. The morphology and crystal phases of the film were controlled and the photocatalytic activity was studied for photocatalytic hydrogen generation. Moreover, we found that Au nanoparticles deposited on a TiO_2 mesocrystal film induced visible light-driven photocatalytic activity, which shows great potential for practical applications.

2. Experimental

2.1. Chemicals and materials

TiF_4 , NH_4NO_3 , chloroauric acid, Na_2SO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ were purchased from Aladdin (AR, Shanghai, China). P123 (amphiphilic triblock copolymer PEO-PPO-PEO $((\text{EO})_{20}(\text{PO})_{70}(\text{EO})_{20})$) and NH_4F (AR) were purchased from Sigma-Aldrich. All the chemicals were used as received.

2.2. Preparation of TiO_2 mesocrystal films

A titanium sheet ($20 \times 30 \text{ mm}^2$) was cleaned by ultrasonic irradiation for 30 min in acetone, ethanol, and deionized water (volume ratio = 1:1:1) after being polished. The precursor solution was prepared from TiF_4 , H_2O , NH_4NO_3 , and P123 (molar ratio = 93:32000:444:1). The TiO_2 mesocrystal films were prepared by titanium sheet dip-coating in the precursor solution. The treated titanium sheets were calcined in air at 300, 400, 500, 600, and 800 °C for 1 h at a heating rate of 5 °C/min, respectively.

2.3. Preparation of Au/ TiO_2 mesocrystal film

Chloroauric acid solution was added to the above precursor solution at contents of 0.5%, 1%, 1.5%, and 2% (mass ratio in Au/ TiO_2). According to the above method, the sheets were calcined in air at 400 °C for 1 h.

2.4. Characterization

The morphology was characterized with a scanning electron microscope (SEM, Hitachi S4800) and a transmission electron microscope (TEM, JEOL JEM-2010). The crystal structure was characterized by X-ray diffraction (XRD, D/MAX-2000 with $\text{Cu K}\alpha$ radiation). The pH value was measured with a pH meter (Mettler Toledo Delta 320). Photoelectrochemical measurements were performed in a conventional three-electrode configuration with an electrochemical station (CHI660). The TiO_2 mesocrystal film was used as the working electrode, and a platinum sheet and saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The transient photocurrent was measured with the use of a 10 s on-off cycle at a bias voltage of 0.5 V or zero in 50 mL Na_2SO_4 solution (0.5 mol/L). UV-Vis diffuse reflectance spectra were recorded with a spectrophotometer (Shimadzu, UV2600) with an integrating sphere attachment in the range 200 to 800 nm and with BaSO_4 as reflectance standard.

2.5. Photocatalytic activity tests

Photocatalytic hydrogen evolution: A double-cell reactor was used for photocatalytic hydrogen generation. The chambers were separated by ion membranes. Two pools were injected with 30 mL ethylene glycol solution (2 mol/L) and 30 mL sodium sulfate solution (0.5 mol/L), respectively. Three electrodes system were used for the hydrogen production tests. The TiO_2 mesocrystal film was used as the working electrode, and a platinum sheet and SCE were used as the counter and reference electrodes, respectively. The photocatalytic hydrogen production was initiated by a xenon lamp with a filter ($\lambda < 400 \text{ nm}$). The amount of H_2 evolved within 1 h of irradiation was determined with a gas chromatograph (Ceauleight, GC-7900).

Photocatalytic reduction of Cr(VI): A Au/ TiO_2 mesocrystal film was immersed in an aqueous solution containing Cr(VI) ions (10 ppm, pH ≈ 3 controlled by HCl), in a home-made reactor stirred for approximately 30 min to reach adsorption-desorption equilibrium in the dark [19,31]. The photocatalytic reduction of Cr(VI) under UV or visible light irradiation was initiated by a xenon lamp with a filter ($\lambda < 400 \text{ nm}$ or $> 420 \text{ nm}$). The concentration of Cr(VI) was analyzed by a UV spectrophotometer (UV 7502/PC) at the characteristic wavelength [32], from which the reduction rate could be calculated as: $(1 - C/C_0)$ (C is the test concentration, C_0 is the initial concentration).

3. Results and discussion

The structure of TiO_2 mesocrystal film annealed at 400 °C was characterized by SEM imaging. The TiO_2 mesocrystal film showed a stacked sheet structure with a size of several micrometers (Fig. 1(a)). A porous structure was clearly observed on the surface (Fig. 1(b)). As we have previously reported, the addition of NH_4F can control the thickness of the resulting TiO_2 plates [19]. Different thickness of the TiO_2 plates can be achieved through the use of different $\text{TiF}_4/\text{NH}_4\text{F}$ contents at the same calcination temperature (400 °C). As the NH_4F content is gradually increased (Fig. 2(a), (b)), the (001) facets of the TiO_2 plates are increased and the resulting crystals become thinner. Many gaps appear between neighboring sheets, which can increase the specific surface area of the films, and are beneficial for the photocatalytic performance. As the amount of NH_4F is increased further (Fig. 2(c)), the TiO_2 plates become very thin resulting in structural collapse. Therefore, the optimum conditions for synthesis of the TiO_2 mesocrystal film were a ratio of $\text{TiF}_4/\text{NH}_4\text{F}$ volume ratio = 1:0.8 and calcination temperature of 400 °C. A cross sectional SEM image (Fig. 2(d)) shows that the

Fig. 1. (a) SEM image of the surface of TiO_2 mesocrystals film; (b) Magnified SEM image of the surface revealing porous structures.

Fig. 2. SEM images of samples at different $\text{TiF}_4/\text{NH}_4\text{F}$ volume ratios: (a) 1:0.4, (b) 1:0.8, (c) 1:1.2, (d) SEM image cross section of (b); (e) TEM image of one falling particle from TiO_2 mesocrystals film; (f) HRTEM images and SAED patterns of (e).

thickness of the TiO_2 crystal layer was approximately $1.33\ \mu\text{m}$. Furthermore, high-resolution TEM (HRTEM) images (Fig. 2(e), (f)) of a particle of the TiO_2 mesocrystals showed that the obtained TiO_2 was a single crystal and highly crystallized, with well-resolved (001) ($d = 0.18\ \text{nm}$) crystalline lattices in selected area electron diffraction (SAED) patterns.

In the annealing process, the precursors of Ti^{4+} , F^- , NH_4^+ , and H_2O undergo a series of reactions during evaporation of water at low annealing temperatures to form NH_4TiOF_3 (see Fig. S2 in Supporting Information (SI)). As the annealing temperature is increased further, NH_4TiOF_3 is easily transformed into TiO_2 . When large amounts of nitrogen and fluorine are removed, the volume of the nanoparticles decreases, and gaps or pores form between the nanoparticles, resulting in porous TiO_2 materials that consist of anatase single-crystalline nanoparticles with dominant (001) facets [18,19]. These TiO_2 nanosheets were assembled onto titanium substrates to form TiO_2 films. These TiO_2 nanosheets have a porous structure. The specific surface area was approximately $50\ \text{m}^2/\text{g}$, and the pore size was mainly concentrated at $20\ \text{nm}$, showing a broad distribution (Fig. S3).

The XRD patterns of the films calcined at $400\ ^\circ\text{C}$ (Fig. 3) indicated that the crystal structures and crystallinity were unchanged by the addition of NH_4F . All the patterns showed strong diffraction peaks from metallic Ti and well-defined characteristic peaks of anatase TiO_2 .

The calcination temperature had a considerable influence on the crystal formation and crystallinity of the prepared TiO_2 mesocrystal film. As shown in Fig. 4, all of the TiO_2 films annealed at different temperatures from 300 to $500\ ^\circ\text{C}$ had

Fig. 3. XRD patterns of TiO_2 film at different $\text{TiF}_4/\text{NH}_4\text{F}$ volume ratios.

well-defined characteristic diffraction peaks of anatase TiO_2 . As the temperature was increased from 300 to $400\ ^\circ\text{C}$, the crystallinity of the TiO_2 film increased. However, when the calcination temperature reached $600\ ^\circ\text{C}$, rutile TiO_2 appeared, and the percentage of the rutile phase increased with increasing temperature.

The morphology of the TiO_2 single crystals changed markedly with increasing calcination temperature. When the calcination temperature ranged from 300 to $500\ ^\circ\text{C}$, the TiO_2 crystals became smaller and thicker (Fig. 2(b), Fig. S1(a), (b)). When the temperature reached $600\ ^\circ\text{C}$, the crystal blocks were damaged, which might have been caused by rapid pyrolysis at high temperature (Fig. S1(c), (d)).

H_2 evolution was used to evaluate the photocatalytic performance of the TiO_2 mesocrystal film. The amount of H_2 evolved increased as the volume ratio of TiF_4 to NH_4F was increased from 1:0 to 1:0.8, and reached a maximum amount of $41.7\ \mu\text{mol}/(\text{h}\cdot\text{cm}^2)$ at a volume ratio 1:0.8. The increased specific surface area and active reaction sites caused by gaps be-

Fig. 4. XRD patterns of TiO_2 film annealed at different temperature ($\text{TiF}_4/\text{NH}_4\text{F}$ volume ratio = 1:0.8).

tween neighboring sheets resulted in this enhancement of photocatalytic H_2 evolution performance (Fig. 5(a)). The H_2 generation performance of the TiO_2 mesocrystal films formed at different calcination temperatures were also investigated, and the results are shown in Fig. 5(b). Owing to the improved crystallinity compared with that of the film obtained at 300 °C, the film calcinated at 400 °C exhibited increased H_2 generation ability. Owing to the optimum calcination conditions and crystalline morphology, the TiO_2 mesocrystal film calcinated at 400 °C demonstrated the best photocatalytic H_2 generation performance. However, the amount of H_2 evolved decreased when the calcination temperature was greater than 400 °C. This decrease was attributed to the appearance of rutile TiO_2 through the phase transformation occurring at high temperature calcination (Fig. 4) and the crushing of crystal blocks (Fig. S1).

Photoelectric measurements were performed to characterize the photoelectric properties of the TiO_2 mesocrystal film. As shown in Fig. 5(c), the photocurrent density increased as the concentration of NH_4F was increased. The TiO_2 mesocrystal film prepared at volume ratio of $TiF_4/NH_4F = 1:0.8$ exhibited the highest photocurrent output of approximately 0.92 mA/cm², which was 3.2 times as high as that of the TiO_2 mesocrystal film with no NH_4F added. However, with more NH_4F

added, the photocurrent output from the films decreased. This was mainly attributed to structural collapse leading to poor contact with the substance. This was also considered to be the main factor leading to the decrease of photocatalytic performance. The photocurrents of the TiO_2 mesocrystal film measured at different calcination temperatures were measured under UV irradiation (Fig. 5(d)). The photocurrent generated by the film calcined at 400 °C was 9 times as high as that calcined at 300 °C. This result reflects the easier migration of photogenerated charge carriers in the film calcined at 400 °C compared with that calcined at 300 °C, owing to the greater crystallinity of the former. As the annealing temperature was increased further, the photocurrent decreased considerably. This decrease was attributed to damage to the structure of the sample and a change of the crystal phase (Fig. 4 and Fig. S1). The results of the photoelectric performance also reflect a change of the photocatalytic performance.

To achieve the visible-light-driven photocatalysis, the TiO_2 mesocrystal film was modified with Au nanoparticles based on the optimized condition described above. The XRD patterns of Au/ TiO_2 films showed that there was no obvious change of the crystalline phase and crystallinity as the Au loading was increased (Fig. S4). Characteristic diffraction peaks of Au were

Fig. 5. Hydrogen production activity of different TiO_2 mesocrystals film under UV light irradiation. (a) Different TiF_4/NH_4F volume ratios, and (b) different calcination temperature; Photocurrent responses of (c) different TiF_4/NH_4F volume ratios and (d) different calcination temperature at a bias voltage of 0.5 V.

Fig. 6. Liquid-phase photocatalytic Cr(VI) reduction on TiO₂ mesocrystals film and 1.0% Au/TiO₂ mesocrystals film under visible light irradiation.

not found in the patterns, which could be attributed to the high dispersion of Au nanoparticles. Furthermore, the addition of Au had almost no effects on the morphology of the films (Fig. S5). The loaded Au nanoparticles induced absorption in the visible spectrum owing to SPR; The absorbance at 500–800 nm gradually increased with the introduction of the Au nanoparticles (Fig. S6). The results of photocatalytic Cr(VI) reduction performance under visible light irradiation are shown in Fig. 6. The reaction system was stirred for approximately 30 min to reach adsorption-desorption equilibrium in the dark. After light irradiation, the Cr(VI) ions were rapidly reduced. Modification of the TiO₂ with Au nanoparticles resulted in an increase of the photocatalytic activity owing to the SPR of the Au nanoparticles.

4. Conclusions

In summary, we prepared TiO₂ mesocrystal films by a direct annealing method. The morphology and crystal phase of the films were controlled by adjusting the ratio of NH₄F and calcination temperature. H₂ evolution was used to evaluate the photocatalytic performance of the TiO₂ mesocrystal film through the use of a three-electrode system. When the volume ratio of TiF₄ to NH₄F was 1:0.8 and the calcination temperature was approximately 400 °C, the H₂ production was 41.7 μmol/(h·cm²). We found that Au nanoparticles loaded onto the TiO₂ mesocrystal film induced highly efficient visible light photocatalytic properties. Our work provides a new highly efficient photocatalytic film electrode, which could be widely applied in photocatalysis and photoelectric catalysis.

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Graphical Abstract

Chin. J. Catal., 2018, 39: 639–645 doi: 10.1016/S1872-2067(17)62980-2

Synthesis of TiO₂ mesocrystal film with enhanced photocatalytic activity

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A TiO₂ mesocrystal film was successfully prepared by a direct annealing method. This new high efficient photocatalytic film electrode could be widely applied in photocatalysis and photoelectric catalysis.

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具有高光催化活性的介孔单晶TiO₂薄膜的制备

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摘要: 光催化技术在常温下能够直接利用太阳能来驱动反应, 已成为一种理想的环境污染治理和洁净能源生产技术. 但是比较多的限制条件阻碍了光催化发展和实际应用, 如何有效解决这些限制因素成为光催化技术走向工业化应用必须解决的问题. 目前光催化材料研究存在的问题主要包括: (1)研究工作主要集中的粉体催化剂存在分离困难、难以重复利用的缺点, 开发与基底结合牢固的薄膜材料是十分必要的; (2)光催化材料本身的光响应范围影响光催化材料的应用, 拓宽催化剂材料的光吸收范围是亟待解决的; (3)光生电子和空穴的复合问题是影响光催化剂催化活性的主要因素之一, 很多方法被用来阻止电子-空穴对的复合, 如: 金属和非金属的掺杂、贵金属修饰、异质结、新型催化剂结构的设计等, 如何设计促进催化剂光生电子和空穴的分离成为光催化技术应用的重要问题.

介孔单晶TiO₂通过自组装的方法被制备, 成为TiO₂的一种新结构材料. 介孔单晶TiO₂结合了介孔材料的大比表面积、单晶材料的电荷传输快等优点, 对于光催化性能有了很大的提高. 目前介孔单晶TiO₂主要是以粉体的形式存在, 但是粉体TiO₂的应用受到多方面的影响, 如: 难回收不易重复利用, 与电催化结合难, 不能借助电催化提高电荷分离效率等. TiO₂薄膜能够解决粉体的不足, 近年来, TiO₂光催化薄膜得到广泛的研究, TiO₂薄膜的制备方法很多, 主要有液相制备方法、物理气相沉积法、化学气相沉积法、电化学方法、溅射法等. TiO₂薄膜主要是以纳米颗粒的形式沉积在基底上, 并且多为多晶和无定形. 而对于介孔单晶TiO₂薄膜的制备和研究还没有报道. 我们通过直接焙烧一步法制备了介孔单晶TiO₂薄膜, 并对TiO₂薄膜的生长情况、表面结构、TiO₂晶相和晶体完整程度的变化对性能的影响进行了研究. 通过调变Ti与F的比例和煅烧温度, 研究不同的制备条件对其性能的影响, 从而制备高活性TiO₂薄膜. 为了进一步提高介孔单晶TiO₂薄膜的活性和拓展其吸收光谱范围, 使用高温热解自组装技术一步法制备了贵金属Au负载的介孔单晶TiO₂薄膜, Au纳米颗粒跟TiO₂有较好的结合度. 在可见光照射下, Au/TiO₂异质结构中Au表面由等离子体共振效应产生的活泼电子会注入TiO₂导带, 使光生电子和空穴得到分离; 同时Au具有特殊的可见光等离子体共振效应能显著改善TiO₂类宽带隙半导体的可见光响应性能.

实验用还原Cr(VI)作为探针反应,考察不同Au含量对光催化性能的影响.

关键词: 介孔单晶TiO₂薄膜; 光催化; 制氢; 六价铬还原

收稿日期: 2017-11-30. 接受日期: 2017-12-13. 出版日期: 2018-04-05.

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基金来源: 国家自然科学基金(21237003, 21407106, 21522703, 213377088); 上海市政府(14ZR1430800, 13SG44, 15520711300); 国际资源化学联合实验室(IJLRC); 中国教育部(PCSIRT_IRT_16R49); 上海市高等学校特聘教授项目(东方学者); 上海市教委曙光计划等项目.

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