



Short communication

Nitrogen-doped anatase titania nanorods with reactive {101} + {010} facets exposure produced from ultrathin titania nanosheets for high photocatalytic performance

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ABSTRACT

To obtain high performance catalysts for the photooxidation of organic pollutants in water, nitrogen-doped TiO₂ nanorods with {101} + {010} facets exposure were successfully synthesized by using ultrathin two-dimensional titania nanosheets as precursor. The nitrogen-doped one-dimensional nanorods had a uniform size within 100 nm. The crystal structure of nitrogen-doped TiO₂ nanorods (anatase) didn't alter even though subjected from morphology transformation, however, their crystallinity improved tremendously, and the exposure and proportion of active facets changed, which synergistically boosted the catalytic efficiency. This integrated technology including modification, morphology and phase control might be indicative for fabrication of advanced photocatalysts to remedy environmental pollutant and produce clean energy in the future.

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1. Introduction

Environmental pollution and energy shortage are the two main challenges which humanity are facing today, and the importance and urgency of developing green and low-carbon technologies to solve is becoming prominent [1,2]. Photocatalysis is one type of green low-carbon technologies and has great potential in the environmental remediation and the development of new energy [3,4]. Among the present photocatalysts, TiO₂-based semiconductor photocatalysts have been the most popular due to its wide applications, such as hydrogen production, solar cells, photoreduction of CO₂ to fuels, sterilization and photocatalysis [5]. TiO₂ is considered as one kind of relatively ideal green photocatalytic materials due to its advantages, such as cheapness, nontoxicity, high stability, reproducibility and recycling utilization [6]. By far, the applied research on TiO₂ for photocatalytic removal of organic pollutants is among the most pursued one [7].

In spite of the above mentioned advantages, the photocatalytic performance of TiO₂ is still influenced by its physicochemical properties like morphology, crystal structure, exposed facets, size and electronic property [8]. Morphology is well correlated with the photo-redox activity of TiO₂ nanocrystals, and it is found that the highest photocatalytic activity can be acquired from shape of nanorod, mainly because of its

unique properties, such as high specific surface area and efficient charge separation [9]. Among the different polymorphs of TiO₂, anatase is found to be the most active phase in photocatalytic processes. Moreover, the intrinsic photocatalytic activity of different facets of TiO₂ nanocrystals are in the order of {101} + {100}/(010) > {101} + {001} + {100}/(010) > {101} > {001} [10]. As for the relation between photocatalytic performance and size of TiO₂ nanocrystals, it is reasonable that the smaller the size, the larger the specific surface area and the stronger the quantum size effect can be, thus the more active the catalyst is. Doping modification enables the altering of electronic structure, and especially, a certain amount of nitrogen-doping will narrow the wide forbidden band to enhance the solar energy usage [11–13].

Numerous scholars devote great efforts on the engineering of TiO₂ nanocrystals either by modification or combination, morphology and crystal structure control to obtain high performance catalysts [14–16]. In this communication, an integrated approach was explored to achieve all these goals. TiO₂ nanocrystals within 100 nm, nanorod-shape, doped with nitrogen, anatase crystal structure with {101} + {010} exposed facets, were successfully fabricated and the results showed that the photooxidative activity for decomposing organic pollutant was boosted greatly compared with its original counterpart i.e. titania nanosheets (abbreviated as TNS). To our best knowledge, it is the first example that an integrated way was applied to combine all the advantages to achieve the photooxidative enhancement of organic dye in water under the irradiation of simulated solar or visible light on nitrogen-doped anatase TiO₂ nanorods with reactive {101} + {010} facets

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(abbreviated as NATNR). We believe that the suggested composite would be an advanced photocatalyst to remedy environmental pollutant and produce clean energy in the future.

2. Experimental

2.1. Catalyst preparation

NATNR was synthesized via hydrothermally treating TNS obtained by solid-state reaction and subsequent exfoliation. Specifically, TNS was prepared through shaking layered $\text{H}_{0.68}\text{Ti}_{1.83}\text{O}_4$ vigorously in tetrabutylammonium hydroxide solution, and $\text{H}_{0.68}\text{Ti}_{1.83}\text{O}_4$ was formed by ion exchange of $\text{Cs}_{0.68}\text{Ti}_{1.83}\text{O}_4$ with H^+ in $1 \text{ mol} \cdot \text{L}^{-1}$ HCl solution after $\text{Cs}_{0.68}\text{Ti}_{1.83}\text{O}_4$ compound was gained by solid-state reaction [17]. Based on TNS, NATNR can be easily fabricated in a facile hydrothermal reaction with the addition of green reagent of urea.

2.2. Catalyst characterization

The morphology of samples was observed by high resolution transmission electron microscope (HRTEM) on Tecnai G2 S-TWIN (FEI, Holland). X-ray diffraction (XRD) patterns were recorded at room temperature with an X'pert PROMPD diffractometer (PANalytical, Holland) with copper $\text{K}\alpha_1$ radiation. X-ray photoelectron spectroscopy (XPS) analyses were tested on an ESCALAB250 (Thermo Scientific, America) with aluminum $\text{K}\alpha$ radiation. Ultraviolet–visible diffuse reflection spectra (DRS) were recorded by a UV-3600 spectrophotometer (Shimadzu, Japan) equipped with an integrating sphere.

2.3. Photocatalytic activity test

The degradation experiments were carried out in a photochemical reactor by using methylene blue (MB) as a model pollutant. A 1000 W Xe lamp positioned in the center of a water-cooled quartz jacket was used to offer simulated sunlight, and visible light ($\lambda > 420 \text{ nm}$) was obtained by a 420 nm cut-off glass filter. At the side of quartz jacket, a 50-mL cylindrical glass vessel was used as the reactive bottle to load reaction solution. The distance between lamp and reactive bottles was 40 mm. In the bottom of the reactive bottle, a magnetic stirrer was equipped to achieve effective dispersion. The temperature of the reaction solution was maintained at $25 \pm 0.5 \text{ }^\circ\text{C}$ by cooling water. 50 mg of NATNR was added into 50 mL of 20 mg/L MB solution to form suspension. Before illumination, the suspension was stirred for 60 min in dark to obtain adsorption equilibrium of MB molecules. At the given time interval, 2 mL of reaction solution was taken out and immediately centrifuged to eliminate the catalyst. The absorbance of filtrate was measured by a spectrophotometer at the maximum absorbance peak of 665 nm.

3. Results and discussion

3.1. Morphology evolution

HRTEM images of exfoliated TNSs are shown in Fig. 1a, c and e, where ultrathin two-dimensional lamellar nanosheets with lateral size about several hundred nanometers can be seen clearly, just like soft silk with wrinkles and folds. The weak lattice fringes with spacing of 0.35 nm for {101} face and 0.19 nm for {200} face of anatase TiO_2 can be observed from Fig. 1c and e. The diffraction spots shown in Fig. 1g indicated that the obtained TNS is a single crystal. NATNR with reactive {101} + {010} facets was successfully prepared by hydrothermally treating pre-synthesized TNS, the insets in Fig. 1a and b show the schematic shape of TNS and NATNR. Fig. 2b displays a representative TEM overview image of NATNR. The image showed that the morphologies of NATNR are uniform and regular nanorods. The diameters of these nanorods are 15–25 nm, and the lengths range from 45 nm to 100 nm. HRTEM images shown in Fig. 1d and f suggest the development

of a well-defined crystalline structure of NATNR. The lattice spacings are found to be 0.35 and 0.24 nm, respectively. These two planes can be well indexed as {101} and {004} lattice orientations of anatase TiO_2 crystal, respectively. Fig. 1h shows the selected area electron diffraction pattern (SAED) of NATNR. The SAED pattern can be indexed to be the {101}, {004}, {200}, {105}, {204} and {116} diffraction planes of the hexagonal structure of anatase.

Clearly, we have successfully modified the ultrathin TNS, and realized the nanostructure transformation of 2D TNS to 1D NATNR. Interestingly, the crystal type didn't alter in the process, and still kept the single crystal of anatase. However, the SAED pattern of NATNR emerged a set of diffraction rings due to its random orientation compared to its precursor of periodic arrangement of TNS. Meanwhile, the crystallinity was strengthened a lot, implying the potentially improved photocatalytic activity. Available research has proved that 1D morphology of TiO_2 nanorods exhibited higher photoactivity than 2D morphology of TiO_2 nanoplates. Furthermore, according to previous study, the as-synthesized NATNR seems likely to own higher photo-redox activity than the original counterpart TNS due to the unique surface chemistry of {010} facets, which enhances charge separation in the presence of low-energy reductive {101} exposed facets [10,16]. Based on the above results, we predicted that NATNR could be favorable for the photooxidative decomposition of organic pollutants in water (MB served as a model pollutant in this work).

3.2. Structure analysis

The crystallographic structure of a series of samples was detected by XRD technology and the results are shown in Fig. 2a and b. From Fig. 2a, we can observe that $\text{Cs}_{0.68}\text{Ti}_{1.83}\text{O}_4$ presented body-centered orthorhombic symmetry after solid-state reaction. The data for $\text{H}_{0.68}\text{Ti}_{1.83}\text{O}_4$ before delamination into TNS were still consistent with those of body-centered orthorhombic structure, indicating the phase structure was maintained after HCl treatment. Compared with the former two, the whole peak intensity of TNS was greatly reduced due to weak crystallinity. Two small angle diffraction peaks appeared sequentially, which are indicative of a lamellar structure with a gallery height of 1.11 nm and unreacted protonic titanate, respectively. In addition, two minor peaks at 2θ values of 25.3° and 48.0° can be indexed to be {101} and {200} crystal planes of anatase TiO_2 . For NATNR, the peaks at $2\theta = 25.31^\circ, 37.82^\circ, 48.01^\circ, 53.88^\circ, 55.06^\circ, 62.65^\circ$ and 68.72° , which are corresponding to {101}, {004}, {200}, {105}, {211}, {204} and {116} planes of anatase TiO_2 (Ref. No. 01-084-1285). XRD results are well consistent with HRTEM patterns.

To monitor nitrogen doping evolution during the hydrothermal progress, XPS was carried out and the results are displayed in Fig. 2c and d. The high-resolution Ti 2p spectrum of NATNR is presented in Fig. 2c. It can be observed from Fig. 2c that the Ti 2p spectrum of NATNR consists of three peaks. The first Ti 2p_{1/2} peak centered at 463.0 eV and the second Ti 2p_{3/2} peak centered at 457.4 eV are all attributed to oxide (TiO_2). The third Ti 2p_{3/2} peak centered at 456.9 eV is consistent with oxynitride (marked as TiN_xO_y for convenience), implying Ti–O–N and/or Ti–N–O bands appeared [18]. Fig. 2d presented the high-resolution N 1s spectrum of NATNR, the peak at 401.6 eV is assigned to the interstitial N atoms in N–O bands, indicating the interstitial nitrogen doping has occurred. The obtained fact from the analysis of N 1s spectrum is greatly consistent with what revealed from the high-resolution Ti 2p spectrum shown in Fig. 2c. At this point, we are definitely sure that we have successfully fabricated nitrogen-doped anatase TiO_2 nanorods with reactive {101} + {010} facets.

3.3. Optical response and catalytic activity

Fig. 3a displayed the UV–vis absorption spectrum of NATNR and commercial P25 as reference. From the inset, it can be seen that NATNR powder, with the color of light yellow, exhibited stronger absorption than P25 in the whole range of wavelength employed. The

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