

Rice spike-like g-C₃N₄/TiO₂ heterojunctions with tight-binding interface by using sodium titanate ultralong nanotube as precursor and template



Minquan Sun^a, Shuling Shen^{a,b,*}, Zhujun Wu^a, Zhihong Tang^{a,b}, Jiaping Shen^a, Junhe Yang^{a,b}

^a School of Materials Science and Engineering, University of Shanghai for Science and Technology, Shanghai 200093, China

^b Shanghai Innovation Institute for Materials, Shanghai 200093, China

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ABSTRACT

A novel rice spike-like g-C₃N₄/TiO₂ nanowire heterojunctions are fabricated by hydrothermal treating Na₂Ti₃O₇ ultralong nanotubes in the presence of g-C₃N₄. The presence of g-C₃N₄ promotes the hydrolysis of Na₂Ti₃O₇ ultralong nanotubes. The partially replaced O of TiO₂ by N from g-C₃N₄ leads to the formation of a tight-binding interface between one dimensional TiO₂ and two dimensional g-C₃N₄, which is crucial for fast and effective transfer of photogenerated electrons in heterostructured photocatalysts. As a result, the g-C₃N₄/TiO₂ nanowire heterojunctions exhibit excellent visible-light photocatalytic activity. The kinetic constant (k) of g-C₃N₄/TiO₂ (0.024 min⁻¹) for degradation of methylene blue under visible light irradiation is 1.85 and 4 times than that of pure g-C₃N₄ and P25, respectively.

1. Introduction

Photocatalytic technology has been considered as an ideal green technology for solving energy crisis and environmental pollution [1,2]. As conventional semiconductor photocatalyst, TiO₂ has been extensively studied because of its high chemical stability, non-toxicity, low cost and suitable reduction potential for redox reaction and so on [3,4]. But only UV light ($\lambda \leq 387.5$ nm, ~ 4% of the solar spectrum) can excite TiO₂ because of its large band gap of 3.2 eV [5–7]. Meanwhile, high recombination rate of photoinduced holes and electrons results in poor quantum efficiency for TiO₂ photocatalyst. Therefore, the key targets are enhancing its visible-light response and improving the lifetimes of its charge carriers. In order to achieve these goals, various TiO₂-based heterojunctions have been constructed based on energy band engineering [8] to extend the visible light response and restrain the recombination of photoinduced electrons and holes [9–11].

In the past few years, graphitic carbon nitride (g-C₃N₄) with suitable band gap (2.7 eV), cheap precursors and simple synthetic routes have been studied as the most promising visible light-driven photocatalyst [12–14]. Besides, with a soft lamellar polymer structure, g-C₃N₄ can be easily wrapped in other complex surface [15]. By the near coincidence site lattice (NCSL) theory [16], the coincidence site density of g-C₃N₄/TiO₂ heterojunction is much higher than individual g-C₃N₄ or TiO₂ component, which indicates that g-C₃N₄ and TiO₂ are more conducive to form stable heterojunctions. Furthermore, the build-in electric field at the interface of coupled g-C₃N₄ and TiO₂ can not only improve the

separation rate of photogenerated electrons and holes but also extend visible light response of TiO₂. At present, g-C₃N₄/TiO₂ heterojunctions are generally synthesized by direct mixing precursor powders of g-C₃N₄ and TiO₂ or impregnating TiO₂ in g-C₃N₄ precursor and then calcination [15,17–20]. Miranda et al. [17], synthesized g-C₃N₄/TiO₂ composites by impregnating g-C₃N₄ and TiO₂ powder in methanol. They proposed that the morphology of TiO₂ in g-C₃N₄/TiO₂ composites significantly affected the degradation of isoniazid. Zhao et al. [18], prepared g-C₃N₄/TiO₂ photocatalyst by annealing the mixture of g-C₃N₄ powder and titanium tetrachloride. In the product, TiO₂ nanoparticles dispersed on the surface of g-C₃N₄ sheet with a 0D interface. For g-C₃N₄/TiO₂ heterojunctions, large contact interface and strong coupling of components are still aspired. Herein, we report the synthesis of 1D rice spike-like g-C₃N₄/TiO₂ nanowire heterojunctions using Na₂Ti₃O₇ ultralong nanotubes as TiO₂ precursor and template through a simple hydrothermal method. The formation mechanism of 1D rice spike-like g-C₃N₄/TiO₂ nanowires was proposed according to a series of experiments. The photocatalytic efficiency and stability of g-C₃N₄/TiO₂ nanowires heterojunctions were evaluated through the degradation of methylene blue (MB) under visible light irradiation. A possible mechanism to explain enhanced photocatalytic activity was finally proposed. The obtained rice spike-like g-C₃N₄/TiO₂ nanowire heterojunctions with high visible light response and low carrier recombination rate will be widely used in environmental purification, solar cell, fluorescence sensor, etc.

* Corresponding author at: School of Materials Science and Engineering, University of Shanghai for Science and Technology, Shanghai 200093, China.
E-mail addresses: slshen@usst.edu.cn (S. Shen), jhyang@usst.edu.cn (J. Yang).

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2. Experimental section

2.1. Materials

P25 power was purchased from Degussa Co. Ltd, Germany. Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, $\geq 95\%$) was purchased from Aladdin Reagent Company, China. Hydrochloric acid (HCl, 37%), sodium hydroxide (NaOH, $\geq 96\%$) and dicyandiamide ($\text{C}_2\text{H}_4\text{N}_4$, $\geq 98\%$), were obtained from Sinopharm Chemical Reagent Co. Ltd. All the chemical reagents were used in the experiments process without further purification. The deionized (DI) water was used throughout this experiment.

2.2. Synthesis of $\text{Na}_2\text{Ti}_3\text{O}_7$ ultralong nanotubes

The hydrothermal synthesis of $\text{Na}_2\text{Ti}_3\text{O}_7$ ultralong nanotubes was according to literature procedure [21,22]. Typically, 0.2 g of P25 powder was added to 30 mL of 10 M NaOH aqueous solution with continuous stirring for 5 min. Then the slurry was transferred into 50 mL Teflon-lined stainless-steel autoclave with a magnetic stirrer. The autoclave was put inside a silicon oil bath on a heating platform and the reaction temperature was set at 130 °C for 24 h and 500 rpm. After reaction, the autoclave was cooled to room temperature naturally. The precipitate was recovered, washed with distilled water for several times to remove excess NaOH. The obtained product was further cleaned by using 0.1 M HCl solution for three times to produce high purity $\text{Na}_2\text{Ti}_3\text{O}_7$ ultralong nanotubes, and washed again with distilled water for several times until pH = 7.

2.3. Synthesis of $g\text{-C}_3\text{N}_4$

$g\text{-C}_3\text{N}_4$ was prepared by heating dicyandiamide in a muffle furnace at 550 °C for 4 h. After being naturally cooled to room temperature, a faint yellow $g\text{-C}_3\text{N}_4$ was obtained [23,24].

2.4. Fabrication of $g\text{-C}_3\text{N}_4/\text{TiO}_2$ nanowire heterojunctions

A typical fabrication process of $g\text{-C}_3\text{N}_4/\text{TiO}_2$ nanowire heterojunctions was described as following: Firstly, a certain amount of $g\text{-C}_3\text{N}_4$ and $\text{Na}_2\text{Ti}_3\text{O}_7$ ultralong nanotubes were mixed with 30 mL distilled water in a beaker. Then the beaker was placed in an ultrasonic bath for 30 min to obtain a heterogeneous mixture. The mixture was transferred into 50 mL Teflon-lined stainless-steel autoclave. The autoclave was maintained at 200 °C for 4 h in an oven. Finally, $g\text{-C}_3\text{N}_4/\text{TiO}_2$ nanowire heterojunctions were obtained. $g\text{-C}_3\text{N}_4/\text{TiO}_2$ nanowire heterojunctions with different mass ratios of $g\text{-C}_3\text{N}_4$ to TiO_2 ($m_{g\text{-C}_3\text{N}_4}:m_{\text{TiO}_2} = 0.2, 1, 5$ and 8) were synthesized and labelled as CTNH-0.2, CTNH-1, CTNH-5, CTNH-8, respectively.

2.5. Characterization

The crystalline phases of the samples were identified by using X-ray powder diffraction (XRD) techniques (Bruker D8 Advance diffractometer) operating with Cu $\text{K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at a scan rate (2 θ) of 3° min⁻¹. The scan range is from 10° to 70°. The morphologies of the samples were characterized by using a field emission scanning electron microscope (SEM, Hitachi S4800), and a Tecnai G2 F30 S-Twin transmission electron microscope (TEM, FEI, USA). X-ray photoelectron spectroscopy (XPS) was measured on a PHI-5000 VersaProbe instrument with Al $\text{K}\alpha$ X-ray source. The Fourier transform infrared spectra (FT-IR) of the samples were obtained with a PerkinElmer spectrum 100 of USA, in which KBr was used as diluents. UV-Vis diffuse reflectance spectra (UV-Vis) were recorded on a PerkinElmer Lambda750 spectrophotometer with wavelength range from 250 to 800 nm.

2.6. Photocatalytic reaction

Photocatalytic activity of the prepared $g\text{-C}_3\text{N}_4/\text{TiO}_2$ nanowire heterojunctions was assessed by the degradation of methylene blue (MB) aqueous solution under visible light irradiation. In a typical experiment, 40 mg of sample was dispersed in 100 mL of MB aqueous solution (10 mg/L) in a reactor. Firstly, the suspension was placed in the dark for 50 min to ensure an adsorption/desorption equilibrium between the catalyst surface and MB molecules. Secondly, the suspension was irradiated under a 300 W Xenon lamp (Perfect Light, PLS-SXE300C/300CUV) with a 420 nm cutoff filter ($\lambda \geq 420 \text{ nm}$). Furthermore, 3 mL liquid samples was acquired at certain time intervals and immediately filtered to separate liquid samples from solid catalyst. Finally, the concentrations of MB before and after reaction were monitored by measuring the absorption band of MB (663 nm) using a Lambda750 UV-vis spectrophotometer. The degradation efficiency was evaluated according to C/C_0 (C_0 is the density of dyes after adsorption equilibrium; C is the density of dyes after reaction).

3. Results and discussion

3.1. Morphology and composition analysis

XRD patterns of sodium titanate, pure $g\text{-C}_3\text{N}_4$ and samples obtained by hydrothermal treating sodium titanate and $g\text{-C}_3\text{N}_4$ are shown in Fig. 1. For pristine sodium titanate, the diffraction peaks at 11.1°, 15.8°, 25.2°, 30.2°, 34.4°, 36.9°, 39.0°, 44.2°, 48.8°, 50.1° and 53.0° are observed, which are corresponding to (100), (200), (011), (300), (−303), (−204), (−401), (−214), (020), (120) and (220) crystal planes of $\text{Na}_2\text{Ti}_3\text{O}_7$ (JCPDS, 59-0666) [25]. Two pronounced diffraction peaks around 12.9° and 27.7° are found in pure $g\text{-C}_3\text{N}_4$ (JCPDS, 87-1526), corresponding to (100) plane of the iner-planar tri-s-triazine unit and the (002) plane of the aromatic systems stacking between the interlayer, respectively [26–30]. It can be found that after hydrothermal treatment of $\text{Na}_2\text{Ti}_3\text{O}_7$ in the presence of $g\text{-C}_3\text{N}_4$, characteristic diffraction peaks of $\text{Na}_2\text{Ti}_3\text{O}_7$ disappear, diffraction peaks of anatase phase TiO_2 (JCPDS, 84-1286) and $g\text{-C}_3\text{N}_4$ appear. With the increase of $g\text{-C}_3\text{N}_4$ content, the intensity of diffraction peaks of $g\text{-C}_3\text{N}_4$ increases and the intensity of diffraction peaks of anatase phase TiO_2 decreases. It indicates that under hydrothermal condition and the presence of $g\text{-C}_3\text{N}_4$, $\text{Na}_2\text{Ti}_3\text{O}_7$ transfer into anatase phase TiO_2 and simultaneously $g\text{-C}_3\text{N}_4/\text{TiO}_2$ heterojunctions form in a strong possibility.

In order to further confirm the formation of $g\text{-C}_3\text{N}_4/\text{TiO}_2$ heterojunctions, SEM and TEM measurements were carried out. Fig. 2a-c firstly shows SEM, TEM and HRTEM images of as-synthesized $\text{Na}_2\text{Ti}_3\text{O}_7$. As shown in Fig. 2a, the $\text{Na}_2\text{Ti}_3\text{O}_7$ synthesized via stirring hydrothermal methods presents ultralong “nanobelt” structure [21]. The length of the ultralong “nanobelt” ranges from hundred micrometers to thousand

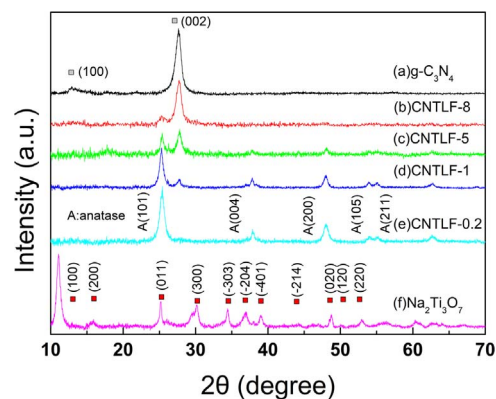


Fig. 1. XRD patterns of (a) $g\text{-C}_3\text{N}_4$, (b) CTNH-8, (c) CTNH-5, (d) CTNH-1, (e) CTNH-0.2 and (f) $\text{Na}_2\text{Ti}_3\text{O}_7$ ultralong nanotubes.

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