



Ti³⁺-TiO₂/g-C₃N₄ mesostructured nanosheets heterojunctions as efficient visible-light-driven photocatalysts



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ABSTRACT

Ti³⁺ self-doped TiO₂/g-C₃N₄ mesostructured nanosheets heterojunctions (Ti³⁺-TiO₂/Meso-g-C₃N₄) have been prepared via calcination-sonication assisted method using amino cyanamide as precursors, combined with a solid-state chemical reduction method. The Ti³⁺-TiO₂/Meso-g-C₃N₄ heterojunctions with narrow band gap of ~2.21 eV possess relative high surface area of ~73.8 m² g⁻¹, and large pore size of ~10 nm. Remarkably, the Ti³⁺-TiO₂/Meso-g-C₃N₄ heterojunctions exhibit excellent visible-light-driven photocatalytic activity for degrading phenol in wastewaters. The photocatalytic hydrogen production rate of Ti³⁺-TiO₂/Meso-g-C₃N₄ heterojunctions rise to ~290.2 μmol h⁻¹ g⁻¹, which is about 4 and 14 times higher than that of the bare Meso-g-C₃N₄ and TiO₂, respectively. The enhanced photocatalytic activity may be ascribed to the synergetic effect of the mesoporous structure providing sufficient surface active sites, and Ti³⁺ self-doping and the formed heterojunctions promoting the spatial separation of photogenerated electron-hole pairs.

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1. Introduction

Semiconductor photocatalysis has been proved to be efficient in mitigating the environmental issues and energy crisis, which refers to photocatalytic hydrogen production [1], solar energy cells [2], pollution degradation [3], as well as bio catalytic [4]. In 1972, Fujishima and Honda published a pioneer work about titanium dioxide (TiO₂), which could split water into hydrogen gas under visible light irradiation [5]. Ever since, excellent qualities, such as commercial availability [6], low toxicity [7], high physicochemical stability [8–10], excellent redox ability as well as benign photocatalytic performance make TiO₂ drawn ever unprecedented attention as a fascinating semiconductor photocatalyst [11,12]. Nevertheless, its photocatalytic performance also gains the invalidation owing to the relatively wide band gap of ~3.2 eV for anatase TiO₂, which seriously inhibits the photo-induced redox reaction [13,14]. Therefore, it is essential not only to present a logical approach to widen photo-response range of TiO₂ but also to restrict the photogenerated carrier recombination.

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To address these limitations, enormous efforts have given to synthesize the modified TiO₂, for instance, metals species/non-metal-doped semiconductor, noble metal deposition, the construction of mesostructure, coupling of composite semiconductors and so on [15–18]. However, those two species impurity doping will add impurities, consequently suppresses the photocatalytic performance. Recently, Mao et al. prepared Ti³⁺ self-doping black TiO₂ by a high-pressure hydrogenation method [19]. Ti³⁺ self-doped TiO₂ strengthened the photocatalytic performance in visible light region because the local states were shaped at the bottom of the conduction band (CB) of TiO₂ by inducing Ti³⁺ or oxygen vacancies (Ov) into the lattice [20]. In addition, the electrical conductivity of the TiO₂ will be strengthened and the transfer of photogenerated charge carriers will be facilitated by introducing Ti³⁺. Furthermore, building heterostructures combining the TiO₂ with other appropriate semiconductors is the effective way to facilitate the mobility efficiency of photogenerated charge carriers, and result in enhanced photocatalytic hydrogen production [21].

Among the numerous semiconductors, graphitic carbon nitride (g-C₃N₄), which is the first to propose to split water into H₂ by Wang in 2009, has emerged as one of the most attractive themes due to the narrow band gap of 2.70 eV and its tri-s-triazine (C₆N₇)-based construction which is highly stable at high tempera-

tures and chemical attack [22–24]. And it is highly appreciated that the effective combination of TiO₂ and g-C₃N₄ can endow the composites with unique characteristics, which shows remarkable effects to photocatalytic activity. The TiO₂/g-C₃N₄ was studied to the photocatalytic hydrogen production by Qu et al. [25]. The TiO₂/g-C₃N₄ hybrid structures exhibited remarkable improvement on the photocatalytic activity for H₂ generation in both visible light and UV–visible light irradiation, which was attributed to the effective interfacial transfer of photogenerated electrons and holes between g-C₃N₄ and TiO₂. Meanwhile, Ti³⁺ self-doped TiO₂/g-C₃N₄ heterojunctions shows excellent photocatalytic efficiency in visible light irradiation than that of the pure g-C₃N₄ and Ti³⁺-TiO₂ [26].

However, the bulk g-C₃N₄ possesses low specific surface area (<10 m² g⁻¹), poor quantum efficiency, and higher photoinduced charge carrier recombination ratios [27,28]. But compared with bulk g-C₃N₄, mesoporous g-C₃N₄ possesses larger surface area and higher efficiency of charge separation [29,30]. The mesoporous g-C₃N₄ was fabricated via the template-calcination method by Wang et al., and the results demonstrated that the photocatalytic H₂ evolution was enhanced nearly 10-folds [31]. Hence, it is crucial to further boost the photocatalytic activity of pure mesoporous g-C₃N₄ by combining Ti³⁺-TiO₂ to form composites, which the composites materials can also offer more surface active sites, and contribute to the diffusion for the reactants and products.

Herein, a novel Ti³⁺-TiO₂/Meso-g-C₃N₄ heterojunctions has been successfully prepared by facile calcinations-sonication assisted method. Moreover, the prepared photocatalyst shows conspicuous photocatalytic performance for removing phenol and splitting water to produce H₂ under visible light illumination. Furthermore, the possible photocatalytic mechanism of Ti³⁺-TiO₂/Meso-g-C₃N₄ heterojunctions is also proposed in this study.

2. Materials and methods

2.1. Materials

The amino cyanide aqueous solution (50 wt%), melamine, 40% hydrofluoric acid (HF), and the silica colloidal solution (LUDOX HS-40, 40 wt% suspension in H₂O) were all purchased from Sigma-Aldrich. TiO₂ (P25, 80% anatase and 20% rutile) power was purchased from Degussa Co. Ltd, Germany. Sodium boron hydride (NaBH₄, 98%) was purchased from Aladdin Reagent Company, China. Absolute ethanol (EtOH) and H₂SO₄ aqueous solution, were purchased from Tianjin Kermel Chemical Reagent Co. Ltd, China. Phenol was purchased from Tianjin Damao Reagents Factory. All of the reagents used in the experiments were analytical grade and employed without further purification, and the deionized water was used throughout the study.

2.2. Synthesis of Meso-g-C₃N₄ nanosheets

The Meso-g-C₃N₄ was prepared via template-calcination process. Typically, amino cyanide solution was dissolved in dispersion of SiO₂ nanoparticles of 12 nm, and then vigorously stirred in a fume hood for 24 h. The well-mixed solution was placed into oven dried at 60 °C until most of the water was evaporated. Then, the resulting white powder was directly heated in a ceramic combustion boat, which was annealed at 550 °C for 4 h with a ramp rate of 2.3 °C min⁻¹ and tempered for an additional 2.5 h. The resulting light yellow powder was treated with 200 mL of 1 M HF for 24 h, and then complete removal of silica template by centrifugation at 4000 rpm and washing with the deionized water and ethanol for three times respectively. Finally, the resultant powders were dried at 120 °C overnight. The ultimate yellow powder was denoted as Meso-g-

C₃N₄. For comparison, the bulk g-C₃N₄ samples were prepared by heating melamine from the room temperature to 550 °C with a ramp rate of 2.3 °C min⁻¹ for 4 h in a muffle furnace, and kept at 550 °C for 2.5 h.

2.3. Fabrication of Ti³⁺-TiO₂/Meso-g-C₃N₄ nanosheets heterojunctions

The Ti³⁺-TiO₂/Meso-g-C₃N₄ nanosheets heterojunctions have been fabricated by facile calcinations-sonication assisted method as follows. Firstly, 0.3 g of the as-synthesized Meso-g-C₃N₄ powder was dispersed into an appropriate amount of ethanol in the beaker and then it was placed in an ultrasonic bath for 90 min to completely disperse the Meso-g-C₃N₄. In the meantime, an appropriate amount of P25 were dissolved into ethanol under ultrasonic treatment for 90 min to obtain a homogeneous suspension. Next, TiO₂ solution were dispersed in the Meso-g-C₃N₄ solution drop wise with magnetic stirring for 48 h to form a uniform solution. After ethanol vaporization, the powder was obtained after drying at 120 °C for 12 h. The final products were collected into porcelain boats to anneal at 200 °C for 2 h under an N₂ atmosphere. The final products were collected without further treatment. The light yellow powder was TiO₂/Meso-g-C₃N₄. Subsequently, 1.5 g of the prepared samples were mixed with 0.75 g of NaBH₄ at ambient temperature, and the mixtures were thoroughly ground for 60 min. The mixtures were transferred into porcelain boats, deaerated under inert gas flow (Ar) for 0.5 h, subsequently, placed in a tubular furnace to anneal at 350 °C for 2.5 h under an Ar atmosphere at a heating rate of 3.2 °C min⁻¹. After naturally cooling down to ambient temperature, and then washed with deionized water several times to remove unreacted NaBH₄. The ultimate dark grey powders were Ti³⁺-TiO₂/Meso-g-C₃N₄ (Scheme 1).

2.4. Characterization

The as-synthesized samples were confirmed by powder X-ray diffraction (XRD) on a Bruker D8 advance under Cu K α ($\lambda = 1.5406 \text{ \AA}$) radiation. The microcrystalline structure and surface characteristics of the photocatalysts were observed by Scanning electron microscopy (SEM, Philips XL-30-ESEM-FEG) operated at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) images were obtained by (JEM-2100 TEM) electron microscope. Fourier transformed infrared (FT-IR) spectra were obtained using a PerkinElmer spectrum between 3900 and 400 cm⁻¹. X-ray photoelectron spectroscopy (XPS) was done on a PHI-5700 ESCA system with Al K α X-ray source. Specific surface areas and pore structures were tested by Brunauer-Emmett-Teller (BET) at liquid nitrogen temperature, using AUTOSORB-1 instrument. UV–vis diffuse reflectance spectroscopy (UV-DRS) was obtained on a UV-2550, Shimadzu UV–vis spectrophotometer, using BaSO₄ as a reference. The electrochemical impedance spectroscopy (EIS) was carried out a computer-controlled IM6e Impedance measurement (Germany).

2.5. Photocatalytic degradation

The activity of the photocatalysts were examined by the degradation reaction of phenol aqueous solution (10.0 mg L⁻¹) under the irradiation of a 300 W xenon lamp with a 420 nm cutoff filter providing visible light irradiation. Typically, 15 mg catalyst powders were added into a glass beaker with 50 ml phenol aqueous solution. Before irradiation, the suspensions were magnetically stirred in the dark for 0.5 h to establish adsorption-desorption equilibrium between phenol aqueous solution and the as-synthesized samples. At irradiation time intervals of every 30 min, 5 mL suspensions were collected, centrifuged and filtrated. The phenol concentra-

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