Applied Catalysis B: Environmental 230 (2018) 260–268

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

One-step synthesis of nanostructured g-C_3N_4/TiO_2 composite for highly enhanced visible-light photocatalytic H_2 evolution

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ARTICLE INFO

Keywords:
g-C_3N_4
TiO_2
nanocomposite
photocatalysis
hydrogen evolution

ABSTRACT

Improving the photocatalytic property of g-C_3N_4 by combined strategies has attracted increasing attention recently. In this work, we realized the structure nanosizing of g-C_3N_4 and its synchronous compounding with TiO_2 nanoparticles in one step, using a facile melamine-involved vapor deposition method coupled with a simple and easy setup. Nanostructured g-C_3N_4/TiO_2 heterojunction was well-established and the resultant nanocomposite demonstrated an excellent visible-light photocatalytic H_2 evolution performance 10.8 times higher than that of bulk g-C_3N_4. The structure nanosizing coupled with the heterojunction construction contributed together to the improvement of photoinduced electron-hole separation and final photocatalytic efficiency. The proposed simple method and setup have the potential to be used for preparing other g-C_3N_4-based nanocomposites with advanced photocatalytic properties.

1. Introduction

Environmental pollution and energy crisis are two major problems to be solved at present [1–3]. Hydrogen energy, a kind of clean energy, has attracted close attention from governments and scientists all over the world [4–6]. Photocatalytic water splitting is considered as an ideal technique for hydrogen production [7]. Among all the catalysts, nanostructured TiO_2 has been extensively studied and commercialized already, e.g. P25 [8]. However, TiO_2 only absorbs little solar photons (~5%) and hardly responds to visible light due to its large band gap of 3.2 eV [9,10]. In recent years, graphitic carbon nitride (g-C_3N_4) has been a topic of wide concern owing to its unique electronic structure and properties [11,12]. Its narrow band gap of 2.7 eV and strong visible-light absorbing ability of 460 nm make it perform well in photocatalysis [13,14]. Nevertheless, the high photogenerated electron-hole recombination rate still limits the photocatalytic efficiency.

Nano-structuring [15–17], element-doping [18,19], composite-constructing [20–22], etc. are useful strategies to improve the activity of catalysts in photocatalytic H_2 evolution. Nano-structuring primarily increases specific surface area of photocatalysts, and element-doping and composite-constructing mainly alters the electronic structure. In general, different strategy contributes in different way to improve a certain aspect of catalyst's properties [23]. Thus, the combination of multifold strategies could bring additive effect on the improvement of photocatalytic activity and becomes a new tendency in the design of advanced photocatalysts [24,25].

Over the years, constructing the composite of g-C_3N_4 and nano-TiO_2 has been proved useful to obtain enhanced performance in photocatalysis, benefiting from their appropriate band levels [26,27]. For example, Zhong et al. successfully designed a g-C_3N_4/TiO_2 heterostructure by calcining the mixture of melamine and TiO_2 nanobelt, where 2 times higher performance of H_2 evolution are obtained [28]. Wang et al. synthesized g-C_3N_4/TiO_2 by calcining their precursors, where 6 times higher performance of H_2 evolution are obtained [29]. However, the g-C_3N_4 phase of these composites is still bulk g-C_3N_4 in the micron size range. It is supposed that, if nanosized g-C_3N_4 is compounded with nano-TiO_2, the resultant nanostructured g-C_3N_4/TiO_2 composite will have a further increased efficiency in photocatalytic H_2 evolution. Several researchers have investigated the synthesis of nanostructured g-C_3N_4/TiO_2. For instance, Chen et al. controlled the growth of g-C_3N_4 on mesoporous TiO_2 spheres, resulting in a better fused g-C_3N_4/TiO_2 heterostructure [30]. Su et al. loaded g-C_3N_4 nanodots on TiO_2 nanotube arrays for better efficiency of pollutant degradation under solar light [31]. Nevertheless, the reported processes for synthesizing nanostructured g-C_3N_4/TiO_2 are generally complex, requiring two or more steps to realize the nano-structuring of g-C_3N_4

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https://doi.org/10.1016/j.apcatb.2018.02.056
Received 24 December 2017; Received in revised form 6 February 2018; Accepted 25 February 2018

and its recombination with nano-TiO_2. Moreover, the photocatalytic H_2 evolution of the nanostructured g-C_3N_4/TiO_2 was not investigated yet and the potential influence has not been revealed. Therefore, it is still of great interest and urgency to realize the facile synthesis of nanostructured g-C_3N_4/TiO_2 composites for enhanced photocatalytic H_2 evolution.

Herein, we proposed and demonstrated a facile one-step method to achieve the nano-structuring of g-C_3N_4 and its compounding with commercialized TiO_2 nanoparticles (P25). The method was actualized via vapor deposition using an easy and simple setup. The as-obtained nanostructured g-C_3N_4/TiO_2 realized 10.8 times higher efficiency than bulk g-C_3N_4 in visible-light H_2 evolution. The detailed process was introduced, the comprehensive characterization of catalysts was conducted and the mechanism of photocatalytic activity improvement was revealed.

2. Experimental

2.1. Materials synthesis

2.1.1. Nanostructured g-C3N4/TiO2 composite

The one-step vapor deposition of nanostructured g-C_3N_4 onto TiO_2 nanoparticles was carried out using an easy and simple setup as illustrated in Scheme 1. It comprises of a covered crucible (300 mL) with a cylinder (4 cm in height) inside. In a typical experiment, 0.5 g TiO_2 nanoparticles (commercialized P25) were placed on the top of the cylinder and 24 g melamine was loaded on the bottom of the crucible. The covered crucible was put in a muffle furnace, heated at 520 °C for 4 h using a heating rate of 15 °C min^{-1} and cooled down naturally. After the above one-step treatment, the white TiO_2 powder on the cylinder top became a light-yellow powder, namely the nanostructured g-C_3N_4/TiO_2 composite. It is supposed that, yellow g-C_3N_4 grew on the surface of TiO_2 nanoparticles although they were not in touch with melamine, resulting from the sublimation feature of melamine and the gaseous phase reaction essence of polymerization reaction from melamine to g-C_3N_4 [32,33]. Different amount of melamine (4.0, 8.0, 16.0, 24.0, 30.0 and 48.0 g) were used in the experiments to adjust the amount of g-C_3N_4 depositing on TiO_2, and an increased melamine dosage leaded to an increased g-C_3N_4 deposition. The resultant products were denoted as CN/TiO_2-x, where x (= 4, 8, 16, 24, 30 or 48) represents the melamine dosage.

2.2. Control samples

For comparison, bulk g-C_3N_4 (denoted as bulk-CN) was collected from the bottom of the crucible. The nanosized g-C_3N_4 phase (denoted as nano-CN) of the g-C_3N_4/TiO_2 composite was obtained by dissolving the TiO_2 phase of CN/TiO_2-24 in hydrofluoric acid aqueous solution (40 wt%) at room temperature. A physical mixture sample of nanosized g-C_3N_4 and TiO_2 was prepared by mixing 0.051 g nano-CN with 0.049 g P25 (denoted as CN/TiO_2-mixture), which owns a weight ratio of nanosized g-C_3N_4 to TiO_2 equal to that of CN/TiO_2-24. Bulk g-C_3N_4/TiO_2 composite (denoted as bulk-CN/TiO_2) was prepared by calcining the mixture of 2 g melamine and 1 g P25, resulting in a weight ratio of g-C_3N_4 to TiO_2 similar to that of CN/TiO_2-24. A physical mixture sample of bulk g-C_3N_4 and TiO_2 was prepared by mixing 0.051 g bulk-CN with 0.049 g P25 (denoted as bulk-CN/TiO_2-mixture).

2.3. Characterization

X-ray diffraction (XRD) patterns of the samples were obtained over the diffraction angle (2θ) of 3–80° by an X-ray diffractometer with Cu Kα radiation. Fourier transform infrared (FT-IR) spectra were acquired on a Nicolet 6700 spectrometer with KBr pellet. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images and the selected area electron diffraction (SAED) pattern were observed on a Tecnai G2 F20 S-TWIN electron microscope with an accelerating voltage of 200 kV. Nitrogen adsorption/desorption isotherms at 77 K were measured on a Micromeritics TriStar 3020 porosimeter. Specific surface areas of samples were calculated by the Brunauer-Emmett-Teller (BET) method. Photoluminescence (PL) spectra were obtained on an F-4500 FL spectrometer (excitation wavelength = 380 nm). UV-visible diffuse reflectance spectra (UV-vis DRS) were recorded by a Shimadzu UV-2500PC UV–vis spectrometer with the wavelength range of 240–850 nm. The photocurrent analysis was measured using photocatalyst-coated fluorine-doped tin oxide (FTO) glass with repeated on-off cycles of Xenon lamp illumination ($\lambda > 420$ nm), which was carried out using a computer-controlled potentiostat and a reference electrode of Ag/AgCl.

2.4. Photocatalytic H_2 evolution

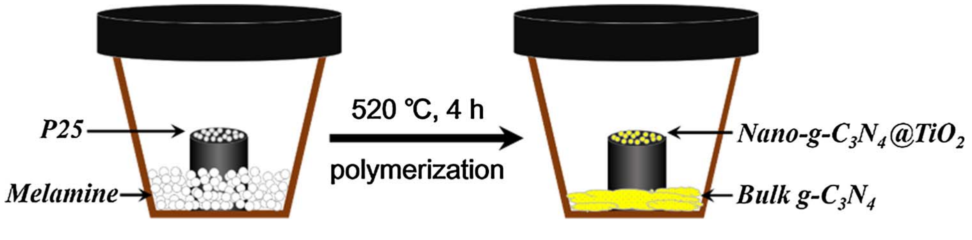
The photocatalytic water splitting reaction was tested in a quartz reactor with top visible light irradiation. Typically, 0.1 g catalyst was dispersed in 100 mL aqueous solution containing 10 vol% sacrifice agent of triethanolamine. Then, under magnetic stirring, 10 mL triethanolamine was added as sacrificial electron donor and 1 mL H_2PtCl_6 aqueous solution was added to preset the mass ratio of Pt cocatalyst to photocatalyst at 3 wt%. The vessel was purged by N_2 for 0.5 h to remove air, sealed with a rubber stopper and then irradiated for 1 h under visible light using a 300 W Xe lamp with a cut-off filter ($\lambda > 420$ nm) at the fixed light-to-liquid distance (10 cm) to photo-reduce H_2PtCl_6 into Pt cocatalyst. Finally, the sealed reactor was irradiated under the same visible light after thoroughly purging the system with nitrogen again, and the reaction temperature was maintained at 283 K by cyclical cooling water. 1 mL gas was sampled every one hour and the hydrogen content was analyzed by a gas chromatograph with a thermal conductivity detector. After reacting for 4 h, the quartz reaction vessel was purged by nitrogen again. The reaction process was repeated for four runs.

2.5. Apparent quantum efficiency (AQE) measurement

The apparent quantum efficiency (AQE) was measured using the water splitting experimental setup under the irradiation of monochromatic light ($\lambda = 420$ nm) and calculated by the formula (1) [34–36]:

$$\mathrm{AQE} = \frac{n\times\Delta G}{I}\times 100\% = \frac{n\times\Delta G}{W\times S\times t}\times 100\% \tag{1}$$

where n stands for the mole number of H_2 evolution; $\Delta G = 237$ kJ mol^{-1}, that is the needed energy of one molecule water



Scheme 1. Schematic illustration of the one-step synthesis of nanostructured g-C_3N_4/TiO_2 composite via facial melamine-involved vapor deposition.