G Model
APSUSC-33515; No. of Pages 10
ARTICLE IN PRESS
Applied Surface Science xxx (2016) xxx–xxx
Contents lists available at ScienceDirect
Applied Surface Science
journal homepage: www.elsevier.com/locate/apsusc

Enhanced visible light activity on direct contact Z-scheme $g-C_3N_4-TiO_2$ photocatalyst

Juan Li [a,b,c], Min Zhang [a,b], Qiuye Li [a,b,*], Jianjun Yang [a,b,*]

[a] National & Local Joint Engineering Research Center for Applied Technology of Hybrid Nanomaterials, Henan University, Kaifeng, 475004, China
[b] Collaborative Innovation Center of Nano Functional Materials and Applications of Henan Province, Henan University, Kaifeng, 475004, China
[c] College of Chemistry and Chemical Engineering, Henan University, Kaifeng, 475004, China

ARTICLE INFO

Article history:
Received 10 May 2016
Received in revised form 22 June 2016
Accepted 25 June 2016
Available online xxx

Keywords:
$g-C_3N_4$ nanosheets
Z-scheme
Nanotube titanic acid (NTA)
Photo-oxidation of propylene

ABSTRACT

Direct contact Z-scheme $g-C_3N_4-TiO_2$ nanocomposites without an electron mediator are prepared via simple annealing the mixture of bulk $g-C_3N_4$ and nanotube titanic acid (NTA) in air at 600 °C for 2 h. In the process of annealing, the bulk $g-C_3N_4$ transformed to ultra-thin $g-C_3N_4$ nanosheets, and NTA converted to a novel anatase TiO_2, then the two components formed a close interaction. The XPS result reveals that some amount of nitrogen is doped into this novel-TiO_2, and $g-C_3N_4$ nanosheets exist in the composites. The results of XRD, TEM and TG indicate that the thickness of $g-C_3N_4$ nanosheets is very thin. The ESR spectrum shows the existence of Ti^{3+} and single-electron-trapped oxygen vacancy in the 30%$g-C_3N_4-TiO_2$ composites. In photocatalytic activity test, the 30%$g-C_3N_4-TiO_2$ nanocomposites showed an excellent photo-oxidation activity of propylene under visible light irradiation ($\lambda \geq 420$ nm), and the removal efficiency of propylene reached as high as 56.6%, and the activity kept nearly 82% after four consecutive recycles. Photoluminescence (PL) result using terephthalic acid (TA) as a probe molecule indicated that the $g-C_3N_4-TiO_2$ nanocomposites displayed a Z-sheme photocatalytic reaction system and this should be the main reason for the high photocatalytic activity. A possible photocatalytic mechanism was proposed on the basis of PL result and transient photocurrent-time curves.

1. Introduction

On account of environment protection, water purification and utilization solar light for hydrogen production from water splitting, photocatalysis has become the research focus of numerous scholars in the world. Among the multitudinous photocatalysts, TiO_2 has been known as a promising photocatalyst because of non-toxic, good stability and strong oxidation ability [1,2]. While the intrinsic imperfection of broad band-gap (3.2 eV for anatase and 3.0 eV for rutile) resulting in only having activity under UV light irradiation and the high recombination rate of photoinduced electrons-holes seriously hindered its practical application [3–5]. Hence it is an urgent problem to explore photocatalysts possessing high activity under visible light in practical application. Many modified methods for TiO_2 have been developed to overcome this problem, such as metal ion doping [6–10], nonmetal doping [11–17], and coupling with narrow band-gap semiconductors [4,18–20].

Graphite-like carbon nitride (denoted as $g-C_3N_4$) with layered two-dimensional planar structure is the most stable crystal form under ambient conditions and has been a hotspot since Wang et al. reported $g-C_3N_4$ could produce hydrogen from water under visible light in 2009 [21]. Although bulk $g-C_3N_4$ has the relative narrow band-gap (2.7 eV) and excellent visible light response, it is seriously confined by high photoinduced electrons-holes recombination rate and small specific surface area (ca 10 m^2/g) in practical application [22,23]. While $g-C_3N_4$ nanosheets possesses the advantages including large specific surface area for providing abundant reactive sites and short bulk diffusion length for reducing the recombination probability of photoexcited charge carriers. The $g-C_3N_4$ nanosheets are mainly obtained by thermal oxidation etching of bulk $g-C_3N_4$ in air [24] or long-time ultrasound exfoliation bulk $g-C_3N_4$ in solvents [25]. For photocatalytic reaction, except for increasing the surface area of the material, improving the separation efficiency is also important. Coupling of two different semiconductors with an appropriate energy band to form the Z-scheme heterojunction structure is a good way to solve this problem. And the Z-scheme multi-components photocatalysts are mainly classified into two kinds: PS-C-PS systems [26] and PS–PS systems [27–33]. The structure of Z-scheme multi-components photocatalysts can facilitate the separation of photo-generated carriers and provide the stronger

* Corresponding authors at: National & Local Joint Engineering Research Center for Applied Technology of Hybrid Nanomaterials, Henan University, Kaifeng, 475004, China.
E-mail addresses: qiuyeli@henu.edu.cn (Q. Li), yangjianjun@henu.edu.cn (J. Yang).

http://dx.doi.org/10.1016/j.apsusc.2016.06.145
0169-4332/© 2016 Published by Elsevier B.V.

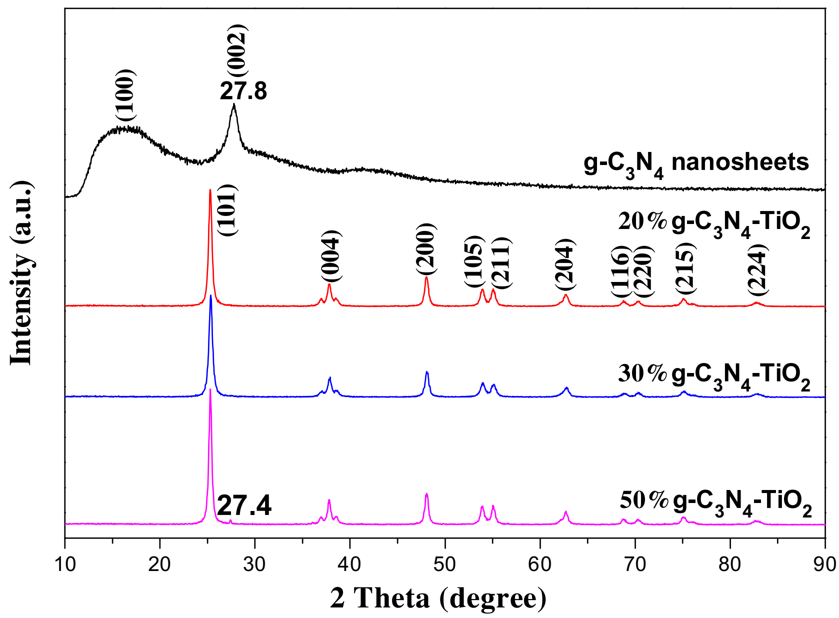

Fig. 1. XRD patterns of the prepared photocatalysts.

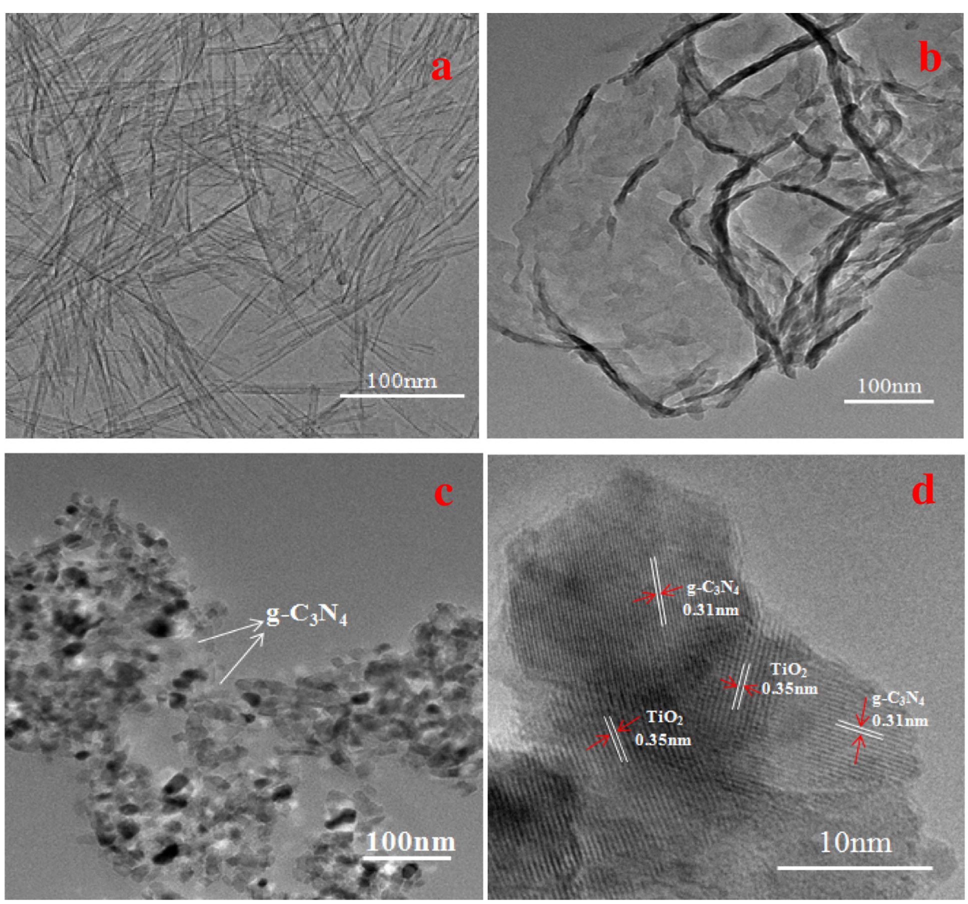

Fig. 2. TEM images of a) nanotube titanic acid (NTA), b) g-C3N4 nanosheets, and c) 30% g-C_3N_4-TiO_2, and High-resolution TEM image of d) 30% g-C_3N_4-TiO_2.

redox ability. Yu et al. prepared a direct g-C_3N_4/TiO_2 Z scheme photocatalyst without an electron mediator by a facile calcination route utilizing cost-affordable P25 and urea as feedstock and its enchanced photocatalytic activities was evaluated by photocatalytic oxidation of HCHO in air under UV light irradiation [19]. Li et al. prepared Ti^{3+} self-doped TiO_2/g-C_3N_4 heterojunctions with high photocatalytic performance under LED light irradiation by calcination the mixture of $H_2Ti_3O_7$ and melamine [5]. According to the reported literature, generally speaking, g-C_3N_4 was excited by visible light to produce the charge carriers, while TiO_2 was only used

Please cite this article in press as: J. Li, et al., Enhanced visible light activity on direct contact Z-scheme g-C_3N_4-TiO_2 photocatalyst, Appl. Surf. Sci. (2016), http://dx.doi.org/10.1016/j.apsusc.2016.06.145