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Graphitic carbon nitride based hydrogen treated disordered titanium dioxide core-shell nanocatalyst for enhanced photocatalytic and photoelectrochemical performance

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ARTICLE INFO

Article history:

Received 24 October 2015

Received in revised form

22 December 2015

Accepted 1 February 2016

Available online 14 March 2016

Keywords:

α -TiO₂/c-TiO₂

g -C₃N₄

Photocatalysts

Photoluminescence

Water splitting

ABSTRACT

Effect of g -C₃N₄ loading on hydrogen treated TiO₂ photocatalyst was studied towards the efficient photocatalytic and photoelectrochemical application. The tailored optical properties and enhanced photoinduced electron-hole separation in crystalline TiO₂ (c-TiO₂) was achieved by creating an amorphous shell (α -TiO₂) around c-TiO₂. The α -TiO₂/c-TiO₂ core-shell particles were further modified by g -C₃N₄ coating, where amorphous α -TiO₂ act as an interlayer between g -C₃N₄ and c-TiO₂ nanocrystals. It was observed that photocatalytic degradation of Methylene Blue (MB) and water splitting to produce hydrogen was remarkably increased under visible-light upon coupling of α -TiO₂/c-TiO₂ core-shell particles with g -C₃N₄ and results in the best MB degradation performance of ~82% in 1 h and water splitting photocurrent density of 450 μ A/cm². The results from UV–vis absorption study, Fourier transform infrared spectroscopy and electron microscopy, photoluminescence, photoelectrochemical measurements and electrochemical impedance spectroscopy suggest that the improved photoactivity is due to the increased light absorption in visible region and efficient charge separation as a result of effective interfacial electron transfer between g -C₃N₄, α -TiO₂ and c-TiO₂ in g -C₃N₄/ α -TiO₂/c-TiO₂ composite.

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Introduction

Efforts are being made around the globe to shift the global energy consumption towards low carbon energy sources. A large number of researches are focussing on processes such as pollutants degradation, hydrogen production by water

splitting etc. via sunlight using semiconductor materials in order to get an overall low carbon emission [1,2]. Nanostructured titanium dioxide (TiO₂) has been considered as one of the most promising semiconductor metal oxide due to its unique properties like high photocatalytic activity, high chemical stability, high photocorrosion resistance, non-toxicity and low cost. However, its high band gap energy

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<http://dx.doi.org/10.1016/j.ijhydene.2016.02.029>

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(3.2 eV) and rapid recombination of photoinduced electron-hole are the main drawbacks in photocatalysis [3,4]. Therefore, it is of great significance to modify the TiO_2 photocatalysts towards visible-light response by enhancing light harvesting, efficient photo-excited charge separation and reducing the recombination of the photo-induced electron-hole pair [5–8]. In reference to these phenomena, enormous research work is nowadays focused on exploiting different strategies to enhance the visible light absorption of large band gap TiO_2 photocatalyst. For instance, sensitization with small band gap semiconductors and band gap narrowing via elemental doping are two versatile approaches shown to improve the conversion efficiency of metal oxide photo-electrodes by modifying their optical absorption coefficient and wavelength [9–11].

Recently, various attempts have been made to increase the photocatalytic efficiency of TiO_2 via chemical modification by doping, ion implantation and surface sensitization using dyes and other semiconductor materials [12–16]. Additionally, much interest has been focused on surface disorders in TiO_2 nanoparticles by hydrogen treatment, which extends its absorption to the visible-light region because of the special electronic band structure. The hydrogen treatment produces black titania, with a crystalline core/amorphous shell structure ($\text{TiO}_2 @ \text{TiO}_{2-x}\text{H}_x$) [17–19]. The black titania showed very strong visible and infrared light absorption, which is believed to be induced by the localized surface plasmon resonance (LSPR) [19]. The LSPR is correlated with high carrier concentration of the amorphous shell. Also, the hydrogen treatment in anatase TiO_2 instigates surface disordering and oxygen vacancies, which leads to the creation of Ti^{3+} centres or unpaired electrons, and subsequently forms donor levels in the electronic structure of anatase TiO_2 [20,21].

The metal-free graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) because of its functionality as a potential visible light photocatalyst, which is owing to relatively rapid photoinduced charge separation in the electron transfer process, high thermal and chemical stabilities and moderate band gap energy of around 2.7–2.8 eV has attracted considerable attention lately [22–24]. Therefore, much interest has been focused on coupling of $g\text{-C}_3\text{N}_4$ as a sensitizer in a composite photocatalyst to prevent the rapid recombination of photoinduced charge carriers. The composite of $g\text{-C}_3\text{N}_4$ with TiO_2 by making $g\text{-C}_3\text{N}_4/\text{TiO}_2$ composites based photocatalyst system has previously been investigated [25–28]. The $g\text{-C}_3\text{N}_4/\text{TiO}_2$ composite forms the type II heterostructure such that the photoinduced charge carriers are easily transferred to their respective bands, i.e. holes tend to pass from the valence band (VB) of TiO_2 to that of $g\text{-C}_3\text{N}_4$, while the electrons pass from the conduction band (CB) of $g\text{-C}_3\text{N}_4$ to that of TiO_2 under irradiation. Chai et al. [27] prepared inorganic composite of $g\text{-C}_3\text{N}_4$ and Pt/TiO_2 with superior photocatalytic H_2 production rate. The authors ascribed such improved H_2 evolution is due to the direct migration of electrons from $g\text{-C}_3\text{N}_4$ to Pt/TiO_2 via close interface and the effective separation of photo-generated charge carriers owing to the developed synergistic effect. Recently, Li et al. [26] investigated the effect of $g\text{-C}_3\text{N}_4$ loading on Ti^{3+} self-doped TiO_2 and they obtained the removal rate constant up to 0.038 min^{-1} with 22.3 wt % Ti^{3+} self-doped $\text{TiO}_2/g\text{-C}_3\text{N}_4$ heterojunction, which was 26.76 times higher than that of pure TiO_2 .

Herein, we prepared novel metal-free $g\text{-C}_3\text{N}_4$ loaded $a\text{-TiO}_2/c\text{-TiO}_2$ nanocomposite (denoted by $g\text{-C}_3\text{N}_4/a\text{-TiO}_2/c\text{-TiO}_2$) by subsequent use of gas-phase and wet-chemical synthesis techniques. The prepared structures of $c\text{-TiO}_2$, $a\text{-TiO}_2/c\text{-TiO}_2$, $g\text{-C}_3\text{N}_4/c\text{-TiO}_2$ and $g\text{-C}_3\text{N}_4/a\text{-TiO}_2/c\text{-TiO}_2$ nanocomposite were investigated for structural, optical and electrical properties. All samples were further investigated for photocatalytic performance under visible-light irradiation ($\lambda > 380 \text{ nm}$). The $g\text{-C}_3\text{N}_4/a\text{-TiO}_2/c\text{-TiO}_2$ nanocomposite exhibited much higher photocatalytic activity for degrading methylene blue than the pristine $c\text{-TiO}_2$, $a\text{-TiO}_2/c\text{-TiO}_2$ and $g\text{-C}_3\text{N}_4/c\text{-TiO}_2$ nanocomposite. The low electron-hole recombination of the prepared $g\text{-C}_3\text{N}_4/a\text{-TiO}_2/c\text{-TiO}_2$ nanocomposite was explained on the basis of photoluminescence (PL) spectroscopy and electrochemical impedance spectroscopy techniques and thus exhibiting high photocatalytic activity under visible light.

Experimental details

Preparation of protonated $g\text{-C}_3\text{N}_4$ sheets

Graphitic Carbon nitride sheets were synthesized via simple heat treatment following the previously reported procedure [23,29]. Briefly, 5.0 g of melamine was annealed at $550 \text{ }^\circ\text{C}$ for 4 h with a heating rate of $5 \text{ }^\circ\text{C}/\text{min}$ and then cool down to ambient temperature in the annealing chamber overnight. Further, the obtained light yellow powder was protonated by post processing treatment with HCl (18.5 wt. %, 50 mL/g of $g\text{-C}_3\text{N}_4$) for 4 h at room temperature. The $g\text{-C}_3\text{N}_4/\text{HCl}/\text{H}_2\text{O}$ suspension is then diluted using 500 mL deionized water and filtered. Finally, the protonated $g\text{-C}_3\text{N}_4$ was washed with deionized water until neutral pH conditions and then dried at $80 \text{ }^\circ\text{C}$ for 4 h. For simplicity, protonated $g\text{-C}_3\text{N}_4$ is denoted as $g\text{-C}_3\text{N}_4$ throughout the paper.

Preparation of $c\text{-TiO}_2$ and $a\text{-TiO}_2/c\text{-TiO}_2$ core-shell nanocrystals

The pristine TiO_2 nanocrystals were synthesized through hydrothermal method by using titanium tetra isopropoxide, nitric acid and deionized water. Specifically, a mixture of 25 mL deionized water and 1 mL nitric acid is added drop-wise with continuous stirring into 10 mL solution of titanium tetra isopropoxide at $0 \text{ }^\circ\text{C}$. This creates a white precipitated solution, which was filtered and heated in air at $80 \text{ }^\circ\text{C}$ to evaporate the excess water. The obtained white powder was annealed at $400 \text{ }^\circ\text{C}$ for 4 h to form the crystalline TiO_2 ($c\text{-TiO}_2$) [33]. Further, for preparation of $a\text{-TiO}_2/c\text{-TiO}_2$ core-shell particle, the prepared $c\text{-TiO}_2$ particles were treated with hydrogen under vacuum condition. 20 sccm 5% H_2 balanced Ar was introduced in the annealing chamber initially at 2×10^{-6} torr pressure and then maintained at 2×10^{-2} torr and $300 \text{ }^\circ\text{C}$ for 30 h.

Preparation of $g\text{-C}_3\text{N}_4/a\text{-TiO}_2/c\text{-TiO}_2$ nanocomposite

The protonated $g\text{-C}_3\text{N}_4$ was ultrasonically dispersed in deionized water for 6 h to get well-dispersed 1 g/mL suspension. Now, 300 mg $a\text{-TiO}_2/c\text{-TiO}_2$ nanocrystals were mixed with 200 mL of deionized water ultrasonically for 60 min. 20 μL

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