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The effect of phosphate modification on the photocatalytic H_2O_2 production ability of g-C_3N_4 catalyst prepared via acid-hydrothermal post-treatment

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ABSTRACT

Protonation of graphitic carbon nitride (g-C_3N_4) based catalyst by acid treatment is proved to benefit for its photocatalytic performance. However, acid-hydrothermal method to synthesize g-C_3N_4 was seldom reported. In this work, phosphate-modified g-C_3N_4 as efficient photocatalyst for H_2O_2 production was prepared via acid-hydrothermal method. XRD, N_2 adsorption, UV–Vis, FT-IR, SEM, XPS, TPD, EIS, and PL were used to characterize the obtained catalysts. Phosphate modification not only influences the morphology, structure property and optical property, but also promotes the O_2 adsorption ability, leading to the improved separation rate of electrons-holes. Phosphate modified g-C_3N_4 catalyst shows the H_2O_2 concentration of 5.4 mmol L^{-1}, more than 13.5 times higher than that of neat g-C_3N_4. The possible reaction mechanism is proposed.

1. Introduction

Environmental pollution and energy crises are two major problems facing humanity. Under this background, heterogeneous photocatalysis has attracted the attention of many scholars in the fields of chemistry, physics, materials science, and environmental protection [1]. An increasing number of semiconductor materials have been found to be suitable for photocatalytic reactions [2–26]. Graphitic carbon nitride (g-C_3N_4), as a metal-free photocatalyst found by Wang et al., has excellent photocatalytic performance in visible light region [27]. Due to the advantages of a suitable band gap, high chemical stability, and unique electronic structure, g-C_3N_4 has shown excellent application prospects in photocatalytic hydrogen production, organic pollutant degradation, organic synthesis, nitrogen fixation, and hydrogen peroxide production [28–33]. However, g-C_3N_4 also suffers from many disadvantages, such as the low visible-light utilization efficiency, high recombination rate, and small BET surface area, which limit its practical application. To advance this promising photocatalyst, many strategies have been applied, such as metal or non-metal doping [34–36], copolymerization [37], semiconductor coupling [38], and nanostructured design [39].

In 2011, Zhou et al. prepared TiO_2 by acid-hydrothermal method [40]. They found that, by controlling the concentration of acid solution, the morphology of as-prepared TiO_2 can be tuned, thus influenced its optical property. In 2013, Zhao et al. prepared TiO_2 catalyst by acid hydrothermal method, and also found that the morphology of the TiO_2 is related to the acid concentration [41]. HCl treated TiO_2 showed the highest salicylic acid and phenol photocatalytic degradation efficiency. In recent years, acid treatment has also been applied to prepare g-C_3N_4 based catalysts. Tong et al. prepared g-C_3N_4 nanosheets by directly adding certain amount of water dropwise into the mixture of bulk g-C_3N_4 and concentrated H_2SO_4 under ambient condition [42]. Compared with bulk g-C_3N_4, the as-prepared g-C_3N_4 nanosheets show great superiority in photogenerated charge separation and transfer, and consequently exhibit significantly enhanced activity in photocatalytic H_2 evolution from water under visible-light irradiation. Tang et al. fabricated several kinds of inorganic acids (H_2SO_4, HNO_3, and HCl) modified carbon nitrides [43]. They found the morphology, porous structure, surface area, and C/N ratio of the catalyst are influenced by inorganic acid treatment. H_2SO_4 treated carbon nitride showed the highest H_2 production ability. However, preparation of g-C_3N_4 by acid-hydrothermal method is seldom reported till now.

Because of the high content of active oxygen (47% w/w) and only H_2O as a by-product, H_2O_2, as a green oxidant, has important applications in many fields such as organic synthesis, water treatment, and catalysis [44,45]. Industrially, H_2O_2 is produced by the anthraquinone method, in which energy consumption is high because of the multistep hydrogenation and oxidation reactions. Thus this method is unsuitable for the current new concept of “green, energy saving and environmentally friendly” in the chemical industry. Recently, the direct synthesis of H_2O_2 from H_2 and O_2 gases has been widely studied using noble metals as catalysts [46,47]. It is considered to be an alternative and green chemistry process. However, this method presents a potential explosion risk from H_2/O_2 mixtures. Recently, photocatalytic hydrogen

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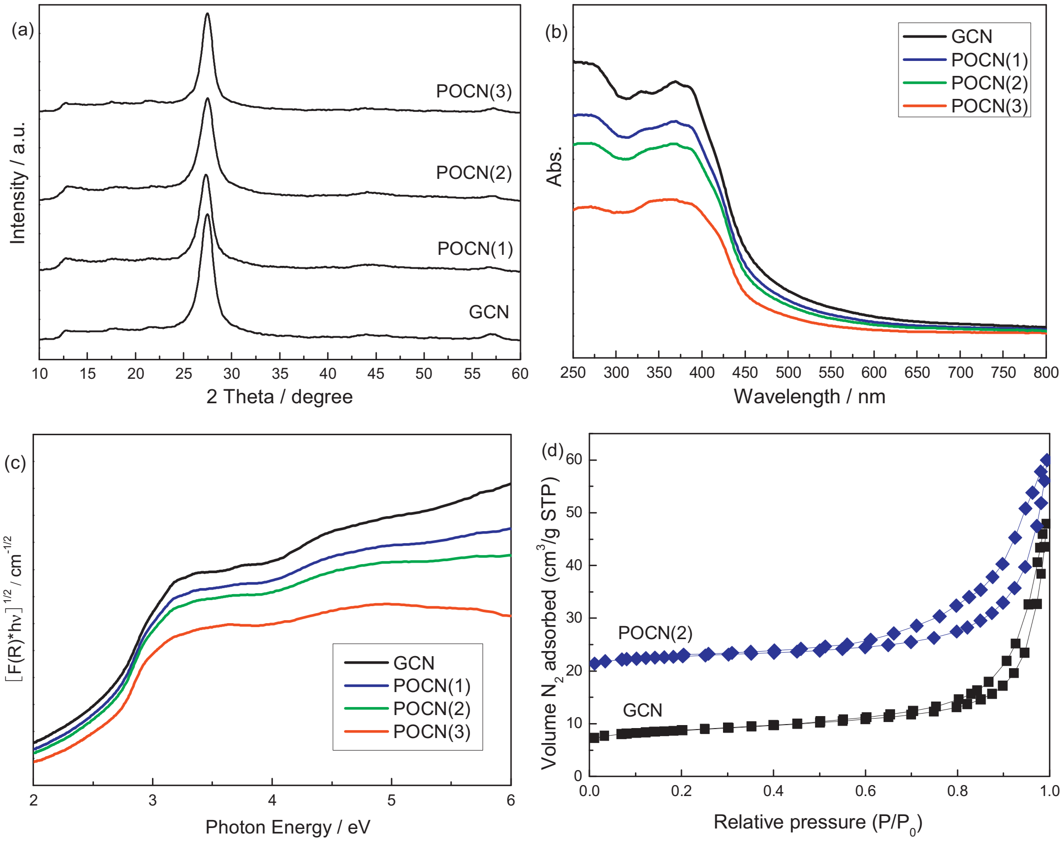

Fig. 1. XRD patterns (a), UV–Vis spectra (b), plots of the transformed Kubelka-Munk function versus the energy of light (c) and N_2 adsorption-desorption isotherms (d) of as-prepared catalysts.

peroxide production technology has attracted a great deal of attention from researchers [48,49]. Hydrogen peroxide is produced by two-electron reduction of oxygen atom. Hydrogen ions come from water. The reaction is shown as follows: $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$. In this work, phosphate-modified g-C_3N_4 with outstanding photocatalytic H_2O_2 production ability is prepared by acid-hydrothermal post-treatment. The influences of acid-hydrothermal treatment on the structural property, optical property, and photocatalytic activity of as-prepared catalyst are investigated in detail.

2. Experimental

2.1. Preparation and characterization

Neat g-C_3N_4 was prepared by annealing melamine at 520 °C for 2 h (at a rate of 5 °C $\min^{-1}$), and denoted as GCN. 2 g of as-prepared GCN was dispersed into 70 mL of deionized water. 10, 20, and 30 mL of H_3PO_4 was added into above suspension under stirring, respectively. The suspension was transferred into a 100 mL Teflon-lined autoclave and maintained at 160 °C for 20 h. The solid was collected by centrifugation, washed with deionized water, and dried at 80 °C. The obtained catalyst was denoted as POCN(1), POCN(2), and POCN(3), respectively.

XRD patterns of as-prepared catalysts were recorded on a Rigaku D/max-2400 instrument using Cu-Kα radiation ($\lambda = 1.54$ Å). The scan rate, step size, voltage, and current was 0.05 °/min, 0.01 °, 40 kV, and 30 mA, respectively. Nitrogen adsorption was measured at −196 °C on a Micromeritics 2010 analyzer. The BET surface area (S_{BET}) was calculated based on the adsorption isotherm. Fourier transform infrared spectra (FT-IR) were obtained on a FT-IR spectrometer (Agilent FTIR-660). UV–vis spectroscopy measurement was carried out on a Agilent Cary 5000 UV–vis spectrophotometer. The morphology of prepared catalyst was observed by using a scanning electron microscope (SEM, SU8010, HITACHI). Temperature programmed desorption (TPD) were performed using a CHEMBET-3000 (Quantachrome, U.S.A.) instrument. Photoluminescence (PL) spectra were measured by FP-6300 fluorospectrophotometer. Xe lamp was used as excitation source. XPS measurements were conducted on a Thermo Escalab 250 XPS system with Al Kα radiation as the exciting source. The electrochemical impedance spectra (EIS) were recorded using an EIS spectrometer (EC-Lab SP-150, BioLogic Science Instruments) in a three electrode cell by applying a 10 mV alternative signal versus the reference electrode (SCE) over a frequency range of 1 MHz to 100 mHz. The cyclic voltammograms were measured in a 0.1 M KCl solution containing 2.5 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1:1) as a redox probe at a scanning rate of 20 mV s^{-1} in the same three electrode cell as the EIS measurement. The photocurrents were measured using an electrochemical analyzer (CHI 618C Instruments) equipped with a rectangular-shaped quartz reactor (20 × 40 × 50 mm) using a standard three-electrode system. The prepared sample film was used as the working electrode, a Pt flake was used as the counter electrode, and Ag/AgCl was used as the reference electrode. A 500 W Xe lamp was used to irradiate the working electrode from the back side. The light intensity on the working electrode was 120 mW cm^{-2}.

2.2. Photocatalytic reaction

The photocatalytic H_2O_2 production ability of as-prepared catalysts was investigated. 0.2 g of catalyst was added into 200 mL of deionized water under stirring to form a suspension. 0.15 g of EDTA was added as a hole scavenger. The experiments were performed in a double-walled quartz reactor. Then, the suspension was exposed to a 250 W high-pressure sodium lamp with main emission from 400 to 800 nm. The UV light portion of the sodium lamp was filtered by $NaNO_2$ solution