



Research Paper

Metal-free black phosphorus nanosheets-decorated graphitic carbon nitride nanosheets with C–P bonds for excellent photocatalytic nitrogen fixation



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ABSTRACT

Visible light photocatalytic nitrogen fixation, as a low-cost and mild technology, needs efforts to explore an economical photocatalyst with high activity and stability. In this study, a metal-free black phosphorus (BP) nanosheets-decorated graphitic carbon nitride nanosheets photocatalyst (BPCNS) has been successfully synthesized. With BP acting as the cocatalyst, BPCNS shows excellent performance in both visible light nitrogen photofixation and pollutant reduction owing to the increased number of excited electrons and enhanced separation efficiency of charge carriers through formation of C–P covalent bonds. Besides, the chemical structure of the BPCNS with optimal content of BP remains the same after exposure to air for 30 days or after five cycles of photocatalytic nitrogen fixation, since the occupation of the lone pairs on phosphorus atoms largely improves the chemical stability of BP.

1. Introduction

Nitrogen fixation is one of the most important reactions in nature since nitrogen (N) is a critical element in building biomolecules [1]. The Haber–Bosch process is used for nitrogen fixation in the industry; however, the Haber–Bosch process needs to consume a large amount of energy due to the harsh reaction condition (300–500 °C and 15–25 MPa) [2]. Therefore, an environmentally friendly method with low energy consumption for nitrogen fixation is highly required. Photocatalysis has great potential in nitrogen fixation as a green and economical technology with solar energy being the driving force in the reaction process [3].

Graphitic carbon nitride (CN), an organic polymeric semiconductor, is regarded as one of the most promising photocatalysts [4]. CN has the advantages of rich raw material, low cost, simple synthesis and visible light response [5], while it also suffers from the limited carrier separation efficiency and limited specific surface area [6]. Exfoliation is an effective method to enhance the catalytic performance of CN. The graphitic carbon nitride nanosheets (CNS) exhibit superior photoelectrical properties on account of large surface area and shortened charge carriers transferring distance [7]. The modification of CN with a cocatalyst, such as Au [8], Ag [9], Pt [10], Pd [11], and their oxides, is another strategy to improve the photocatalytic activity. Though these precious metals show high performance in cocatalysis, their application

is limited by high price and low reserves. Thus, it is a prominent challenge to find cheap cocatalyst with high reserves in the nature. Several metal-free cocatalyst/CN systems have been reported recently with carbon based material (such as carbon quantum dots [12], graphene oxide [13], carbon nanotubes [14] and C₆₀ [15]) as the cocatalyst, while cocatalyst made of other nonmetallic elements are rarely reported.

Phosphorus (P) is one of the most abundant elements on earth. There are several kinds of P allotropes, including white, red and black phosphorus, among which black phosphorus (BP) is the most stable one [16]. Tunable band gap (0.3–2 eV) and high charge-carrier mobility (1000 cm² V⁻¹ s⁻¹) [17] make BP a promising candidate for field-effect transistor [18], lithium battery [19], gas sensor [20], thermoelectric devices [21], super capacitor [22], and et al. However, there has been limited reports introducing BP as a photocatalyst for the oxidation of organic pollutant [23,24], and to the best of our knowledge no research about BP as a cocatalyst has been published so far. In addition, the formation of bonding state between cocatalyst and photocatalyst has not been paid with enough attention. Wu et al. reported the (Co, Fe)–N–C as the active sites for oxygen reduction reaction (ORR) [25]. Recently, Li et al. reported the enhancement of P–Co–N in CoP/CN to photocatalytic hydrogen evolution [26]. The effect of C–P bond between cocatalyst and CN to the catalytic system has not been reported yet. There are ample functional groups on the surface of CNS,

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which is theoretically possible to react with the lone pair electrons of BP to form C–P bonds.

Herein, we synthesized metal-free black phosphorus nanosheets/graphitic carbon nitride nanosheets photocatalyst (BPCNS) with stable C–P bond through a post calcination process for the first time. BPCNS shows remarkably enhanced photocatalytic nitrogen fixation efficiency compared with CNS and Pt/CNS. Besides, we report the effect of C–P in BPCNS on stability and catalytic efficiency for the first time.

2. Experimental section

2.1. Synthesis of BPCNS

Bulk BP was synthesized via a facile low-pressure transport route according to the literature [27]. In a typical synthesis, 500 mg of red phosphorus (99.999%, Aladdin), 10 mg of SnI₄ (99.999%, Sigma–Aldrich), and 20 mg of Sn (99.998%, Sigma–Aldrich) were sealed in a quartz tube under vacuum. The quartz tube was heated up to 923 K at a heating rate of 1.35 K per minute. After keeping at 923 K for five hours, the temperature was reduced to 773 K at a cooling rate of 0.33 K per minute followed by a natural cooling process. The large BP crystals were then carefully collected and kept in a glove box for further use.

The bulk CN was synthesized by direct heating of dicyandiamide (99.5%, TCI) at 823 K for 4 h.

The black phosphorus nanosheets (BPNS) or CNS were prepared through liquid exfoliation of the corresponding bulk sample. In detail, 30 mg of BP or CN was dispersed in 100 mL of water under argon and the suspension was sonicated for 10 h. The nanosheets were finally obtained by centrifugation of the stable suspension at 5000 rpm for 10 min.

A certain volume of the BPNS suspension (0.3 mg mL⁻¹) was added to 100 mL of a CNS suspension (0.3 mg mL⁻¹) and sonicated for 30 min under argon to obtain a stable homogeneous dispersion of the BPNS and CNS. The dispersion was then centrifuged and dried under vacuum to obtain BPNS/CNS. BPNS/CNS was calcined in argon at 573 K for 2 h to acquire the final product BPCNS. The resulting composite catalyst was denoted as xBPCNS, where x is the mass ratio of BP to CNS. A control sample without calcination was prepared and labeled as 0.05BPCNS-WC.

2.2. Synthesis of Pt-CNS

Pt-CNS was synthesized by a photodeposition method. In detail, 500 mg of CNS, a certain amount of H₂PtCl₆, and 10 mL of methanol were added into a quartz reactor with 200 mL of distilled water. The suspension was stirred for 1 h before a 500 W Hg lamp was turned on. After 5 h irradiation, the product was collected by centrifugation. Then the product was washed several times and dried under 333 K. The final product was labeled as xPt-CNS, where x is the mass ratio of Pt to CNS.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (Bruker D8 Advance) using Cu K α ($\lambda = 1.540 \text{ \AA}$). Transmission electron microscopy (TEM) images were performed using JEOL JEM2100. Transmission electron microscopy energy dispersive X-ray analysis (TEM-EDX) mapping was acquired on an aberration-corrected transmission electron microscopy (Titan G2 60-300, FEI). Field emission scanning electron microscopy (FESEM) images were observed on Hitachi S-4800 at an accelerating voltage of 15.0 kV. Atomic force microscopy (AFM) images were obtained on Bruker Dimension Icon microscope. Nitrogen adsorption-desorption isotherms were measured at 77 K using Micromeritics ASAP 2020. The specific surface area was calculated with the Brunauer–Emmett–Teller (BET) method and the pore size distribution of the sample was calculated from desorption branch isotherms. X-ray photoelectron spectroscopy (XPS) and valence

band X-ray photoelectron spectroscopy (VBXPS) measurements were carried out on ESCALAB 25 (Thermo-VG Scientific). The Fourier transform infrared (FT-IR) experiment was carried out on a Nicoletis10 spectrometer (ThermoFisher). The ³¹P cross-polarization magic angle spinning nuclear magnetic resonance (NMR) spectra were recorded with a Bruker Avance 400 spectrometer at room temperature. UV–vis diffuse reflectance spectroscopy (UV–vis DRS) were obtained on the dry-pressed disk samples using UV–vis spectrometer (Evolution 220, ThermoFisher). Photoluminescence (PL) spectra were measured on a FL3-Tcspc spectroscopy (Jobin Yvon). Time-resolved fluorescence decay spectra were obtained with an Edinburgh FLSP920 spectro-photometer with an excitation wavelength of 338 nm. The electron paramagnetic resonance (EPR) measurements were carried out on JES-FA200 (JOEL). Electrical impedance spectroscopy (EIS), linear sweep voltammetry (LSV) and photocurrent transient response were tested with a CHI 660E electrochemical workstation in a standard three-electrode system using the prepared samples as the working electrodes. To prepare the working electrode in LSV experiment, 5 mg of catalyst was mixed with 500 μ L of distilled water, 500 μ L of ethanol, and 80 μ L of 5 wt% Nafion solution with the aid of ultrasonic agitation to form a homogeneous catalyst-Nafion suspension. Then 5 μ L of suspension was dropped onto a glassy carbon electrode (GCE) with 3 mm diameter. LSV was performed in 0.5 M Na₂SO₄ solution after 50 cyclic voltammetry (CV) scans with a scan rate of 5 mV s⁻¹. Potential corrections for the iR drop were applied.

2.4. Visible-light photocatalytic reduction of Cr(VI)

The catalyst (20 mg) was added to 50 mL of 10 mg L⁻¹ Cr(VI) solution consisting of 5 mL methanol and 45 mL purified water. The mixture was kept stirring in the dark for 60 min to reach adsorption–desorption equilibrium before a 500 W Xe lamp was turned on. At given time intervals of irradiation, 1 mL of suspension was withdrawn and filtered to remove all catalyst particles. The concentration of Cr(VI) was evaluated with a high-performance liquid chromatograph (e2685, Waters) equipped with a UV–vis detector (2489, Waters). An XBridge C18 column (4.6 \times 250 mm) from Waters was adopted for separation using methanol and 5 wt% acetic acid aqueous solution (60/40, V/V) as the mobile phase. The flow rate was 1 mL min⁻¹ and the detection wavelength was 285 nm.

2.5. Visible-light photocatalytic nitrogen fixation

The catalyst (30 mg) was added into 50 mL 5 vol% methanol aqueous solution. Nitrogen was bubbled through at a flow rate of 100 mL min⁻¹. The suspension was stirred for 30 min and then the 500 W Xe lamp with a 420 nm cutoff filter was turned on. At given time intervals of irradiation, 2 mL suspension was collected and centrifuged to obtain liquid samples. The concentration of ammonia was determined using Nessler's reagent.

3. Results and discussion

Fig. 1a compares the XRD patterns of BPCNS samples with varying BP contents (1–10 wt%) with patterns for bulk CN and CNS. The XRD pattern recorded for CN has two distinct diffraction peaks: the strong one at 27.4° indexed for graphitic material as the (002) plane represents the interlayer stacking of the conjugated double bonds. The weak diffraction peak at 13.1° is indexed as (100) in JCPDS 87-1526. The XRD pattern of CNS has two consistent peaks with bulk CN, suggesting that the nanosheets basically have the same crystal structure as their parent CN. However, the peak of CNS at 27.4° becomes less pronounced, suggesting the successful exfoliation of CN [28]. The XRD pattern of pure BP has five discernible diffraction peaks, which confirms the orthorhombic structure of BP according to JCPDS 76-1957 [23]. The BPCNS samples with BP contents of 5 wt% and 10 wt% exhibit

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