



Template-free synthesis of porous graphitic carbon nitride microspheres for enhanced photocatalytic hydrogen generation with high stability



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ABSTRACT

Graphitic carbon nitride microsphere photocatalysts were prepared through a template-free solvothermal approach with post-heating treatment. Structural characterization results reveal that the as-prepared sample has the same composition as bulk g-C₃N₄, but appears as hierarchical microspheres with nanoporous surfaces. Comparing to the bulk g-C₃N₄, these porous microspheres exhibit narrowed bandgap and lower resistance, which allows more effective visible-light harvesting and more efficient transport and separation of photogenerated charge carriers. Consequently, we observed high rate of photocatalytic H₂ production and stronger photocurrent responses under visible light irradiation. Further, the long-term photocatalytic test proved high stability of the prepared nanoporous microsphere for H₂ generation.

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1. Introduction

Graphitic carbon nitride (g-C₃N₄) as a metal free polymeric semiconductor has been widely used for photocatalytic H₂ generation because it is non-toxic, low cost, high stability and visible light active [1–7]. However, the photocatalytic efficiency of H₂ generation from proton reduction over polymeric carbon nitride is usually low due to (1) limited visible-light absorption; (2) low efficiency in electron-hole separation; (3) lack of surface active sites for H₂ evolution [8,9]. Inspired by the shape-directed functionality in nanoscale, researchers have reported a variety of photocatalysts with specific morphology and microstructure that improve sunlight harvesting and charge-carrier separation [10–12]. In particular, the hierarchical microsphere has received great attentions for high photocatalytic activity, and promoted mass and charge transport in the packed-bed flow systems [12–14]. Recently, the fabrication of g-C₃N₄ microsphere and hollow structures has been reported by using porous silica spheres as sacrificial templates [14–16]. Nevertheless, considering the complicated process in post-removing silica templates with additional cost, it is still highly

desirable to develop a template-free method for preparing porous microspheres of graphitic carbon nitride.

So far, the major synthetic strategy of graphitic carbon nitride is still based on the higher temperature (>400 °C) annealing of molecular precursors such as melamine and urea, which is non-controllable in the product sizes and morphologies [6,17–20]. In comparison, several groups have demonstrated that the condensation of triazine precursors through solvothermal treatment could also lead to formation of graphitic carbon nitride [21–24], which provided an opportunity to control the specific morphology and microstructure of graphitic carbon nitride at relatively lower temperature.

Herein, in this work, we report template-free synthesis of hierarchical nanoporous carbon nitride microspheres through a solvothermal method. The synthetic process is illustrated in Fig. 1 with two steps: (1) solvothermal preparation of carbon nitride microsphere (CNMS) by using melamine and cyanuric chloride as precursors; (2) annealing of CNMS at 550 °C to obtain g-C₃N₄ microsphere (CNMS-550). For comparison purposes especially in photocatalytic H₂ generation, Pt nanoparticles were decorated on CNMS-550 through a wetness impregnation process. The growth mechanism of the hierarchical microspheres of graphitic carbon nitride was proposed clearly through the time-dependent experiments. The as-prepared samples were characterized in detail by X-ray diffraction (XRD), scanning electron microscopy (SEM),

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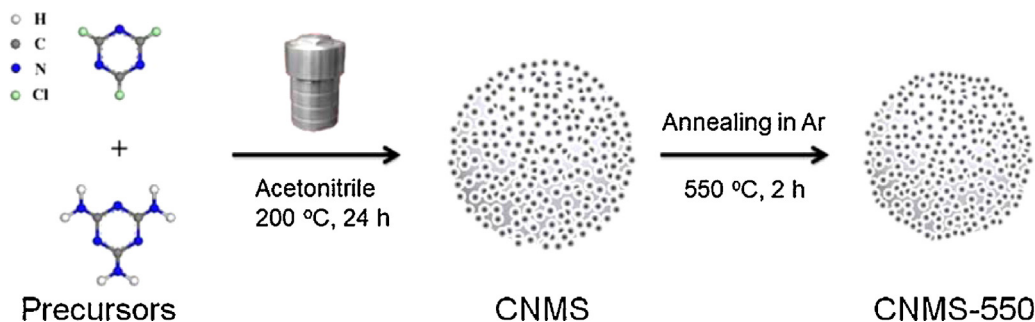


Fig. 1. Schematic illustration for the formation of g-C₃N₄ microsphere.

transmission electron microscopy (TEM), N₂ physical adsorption, Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron (XPS), elemental analysis, and solid-state ¹³C nuclear magnetic resonance (NMR) spectra. Structural characterization results reveal that the as-prepared sample has the same composition as bulk g-C₃N₄, but appears as hierarchical microspheres with nanoporous surfaces. UV–vis spectrum, photoluminescence (PL) spectrum, and photoelectrochemical characterization were used to explore details of light adsorption and conversion, charge separation and transportation of photogenerated electrons and holes in CNMS-550. The hierarchical porous structures of obtained CNMS-550 allow for more effective visible-light harvesting and improve the transport of photogenerated charge carriers from core to surface particulates with effective suppress of radiative charge recombination and thereby enhance the photocatalytic activities.

2. Experimental

2.1. Preparation of graphitic carbon nitride microsphere (CNMS)

All chemicals used in the experiments were reagent grade and no further purification is needed before use. The CNMS was synthesis by solvothermal synthesis. Typically, 54 mg Cyanuric chloride and 18 mg melamine powders were dispersed in 60 ml acetonitrile and then mix solution was put into a 100 ml Teflon-lined autoclave. The mixture was stirred for 21 h, and then the autoclave was sealed and maintained at 200 °C for 24 h. The obtained products were sequentially washed with distilled water and absolute ethanol several. To obtain the g-C₃N₄ like CNMS (CNMS-550), CNMS was calcined at 550 °C under the Ar flowing for 2 h.

Pt nanoparticles loaded samples (3.0 wt%) were prepared by wetness impregnation process. Typically, 40 mg of as prepared samples were first impregnated with 1.0 mg/mL H₂PtCl₆ solutions, followed by the ultrasonic treatment for 5 min. Thereafter, the slurry was dried at 120 °C for 5 h and the obtained solid samples were further treated by NaBH₄ reduction. Final products were washed thoroughly with distilled water to completely remove ions and collected by centrifugation, finally dried at 120 °C.

2.2. Characterizations

The XRD patterns of all samples were collected on XRD-6000 X-ray diffractometer (Cu Kα source) at a scan rate of 2° min⁻¹. SEM images were obtained by JEOL JSM-6340F scanning electron microscope set 5 kV as acceleration voltage. TEM images were obtained by a JEOL model JEM 2010 EX instrument at an accelerating voltage of 200 kV. With Lambda 750 UV/vis/NIR spectrophotometer (Perkin-Elmer, USA) using BaSO₄ as reference, UV–vis diffuse reflectance spectra (DRS) were measured. Fourier transform infrared spectra (FTIR) were derived from Perkin Elmer Fourier Transform Infrared Spectrometer GX. Photoluminescence

(PL) spectra were accomplished in solid with Shimadzu RF5301 Spectrofluorophotometer with an excitation wavelength of 320 nm. For photoelectrochemical experiments, the as-prepared sample was coated on fluorine-doped tin oxide (FTO) glass as the working electrode. Typically, the FTO glass with a size of 1.0 × 2.0 cm was washed in turn with acetone, ethanol, and DI water under continuous sonication, and then dried in N₂ flowing. By dispersing a certain amount of sample in water, the sample slurry was obtained and used for spreading onto the cleaned FTO glass substrate (photoactive area of 0.25 cm²), and dried at room temperature. Uncoated areas on the electrode were isolated with insulating tape. Photocurrent was measured by using the conventional three-electrode electrochemical cell with a working electrode, a platinum wire counter electrode and a saturated calomel electrode (SCE) as reference electrode. The working electrode was immersed in a sodium sulfate electrolyte solution (0.5 M) and irradiated by a visible light. Electrochemical impedance spectroscopy (EIS) and Mott–Schottky curves were carried out on a potentiostat Autolab PGSTAT-30 equipped with a frequency analyser module using a three-electrode system in 0.5 M Na₂SO₄ solution.

2.3. Photocatalytic H₂ evolution

The photocatalytic hydrogen production was carried out in quartz reactor. Typically, 10 mg of the Pt loaded sample (3.0 wt%) was dispersed into 10 mL triethanolamine (TEOA, 15 vol%) aqueous solution. Before the irradiation with visible light, the suspension was degassed with N₂ for 15 min to remove the O₂ in the system. A 300 W Xenon Lamp (MAX-302, Asahi Spectra, USA) with the assistant of UV cut-off filter (λ > 420 nm) was adopted to provide the visible light. The amount of produced H₂ at a regular interval (1 h) was analyzed by gas chromatograph (Agilent 7890A) with TCD detector. All reactions were accomplished at room temperature. The apparent quantum efficiency (AQE) value was calculated according to the equation of $AQE = (2 \times \text{number of evolved H}_2 \text{ molecules} / \text{number of incident photons}) \times 100\%$ [25].

3. Results and discussion

The XRD pattern (Fig. S1) of the obtained CNMS sample shows a clear peak at 27.3° ($d \approx 0.323$ nm) corresponding to the (002) interlayer of graphitic carbon nitride [16,22,26], and a small peak at 17.9° attributed to one of the structural periods in the carbon-nitride layer [27,28]. The morphology and microstructure of the products are shown in Fig. 2. The low magnification SEM image (Fig. 2a) indicates that the products obtained from the solvothermal process are well-defined microspheres with an average diameter of ~2 μm. The enlarged SEM image (Fig. 2b) reveals that the products have hierarchical porous structure consisting of a microsphere core coated with nanoparticles (~10 nm diameter) and short

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