



Facile synthesis of oxygen doped carbon nitride hollow microsphere for photocatalysis



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ABSTRACT

Tailoring defective conjugated heterocyclic network to make for broaden light absorption and efficient charge separation for photocatalytic application is an urgent assignment for graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) materials. Here we report a facile “one-pot” solvothermal method to synthesize controllable O-doped $g\text{-C}_3\text{N}_4$ catalysts at low temperature. By this template-free approach, hollow microsphere O-doped $g\text{-C}_3\text{N}_4$ products were obtained. Structure characterization reveals that the as-prepared sample has incomplete heptazine heterocyclic ring structure, and appears O doping in the lattice, which may derived from the activated O_2 molecular. With the extending condensation time, the increased heteroelement doping content and narrowed band gap promote the light harvesting and charge separation efficiency. Compared to pristine $g\text{-C}_3\text{N}_4$ prepared under high-temperature calcination, this novel material show remarkably photocatalytic activity for environment pollutant purification and splitting water for H_2 evolution, even though the conduction level decrease. This work highlights that the architecture and electronic properties of $g\text{-C}_3\text{N}_4$ based materials could be facile control through mild solvothermal route, which is a reference way for design and fabricate highly efficient non-metal photocatalyst with peculiar feature.

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1. Introduction

Semiconductor-mediated photocatalysis technology has been regarded to be the most appealing methods for environmental pollutant elimination and energy transformation, like degradation of organic pollutants and splitting water to produce hydrogen [1–3]. At present, hundreds of functional materials using as photocatalysts have been developed, such as so many metal oxides, nitrides, sulphides and so on [4–6]. However, the extensive application of photocatalysis in practice still faces huge changes due to the poor quantum conversion efficiency, expensive raw materials and activity instability.

Nowadays, more reaches tend to focus on metal-free catalytic/photocatalytic material, because of its unique advances, such as rich raw material, plenty of modification feasibility, and environmentally friendly. In recent years, binary carbon nitrides (CNs), one of the oldest metal-free polymer, has been regarded as promising

novel green photocatalysts with visible light. Since 2009, $g\text{-C}_3\text{N}_4$ was reported by Wang et al. as an attractive photocatalyst for producing hydrogen from water, the application of this catalyst has been expanded to several fields, like sensors, artificial light synthesis, CO_2 reduction, etc. [7–12]. In order to overcome the inherent restrict of intrinsic carbon nitride materials, so many reach works focus on modification of $g\text{-C}_3\text{N}_4$ to optimize its structure so that to enhance its photocatalytic properties have been done. Up to now, $g\text{-C}_3\text{N}_4$ with diverse nanostructures and morphology obtained from replication of hard templates has been reported. For example, $g\text{-C}_3\text{N}_4$ nanorods and mesoporous spheres used as photocatalysts for hydrogen generation have been successfully synthesized from template-induced method (silicon or molecular sieve) [13–16]. Even so, the complicated synthetic procedures and indispensable corrosive reagent (HF , NH_4HF_2 , etc.) brings the possible risk for preparation and environment. In composition to hard-templating, soft templates make the synthesis process simple and the morphological tuning diversiform. Therefore, soft templating method is more desirable alternation. For many researchers, bubble templating method using urea or thiourea as sacrifice reagent have been reported to obtain porous $g\text{-C}_3\text{N}_4$ [17,18]. However, there are few

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successful works reported on directly use soft molecular for modification of $g\text{-C}_3\text{N}_4$ [19]. Because the molecular of soft template are easily to decomposition and restrain the polycondensation of precursors to $g\text{-C}_3\text{N}_4$ during the high-thermal treatment process, which constraints on the structure optimization.

$g\text{-C}_3\text{N}_4$ is a typical organic polymer, which could synthesized from various organic monomers (cyanamide, melamine, urea, etc.). Traced back to ten years ago, soft chemical methods (solvothermal, $<400^\circ\text{C}$) were often used to synthesize carbon nitride materials. During one-step mobile thermal assembly, $g\text{-C}_3\text{N}_4$ particles with several morphologies were obtained. For example, $g\text{-C}_3\text{N}_4$ sphere was first obtained by Khabashesku et al. through reflux solution reaction of cyanuric chloride and lithium nitride using diglyme as solvent [20]. $g\text{-C}_3\text{N}_4$ nanotube also was synthesized through a catalytic-assembly solvothermal route at 230°C using cyclohexane as solvent [21]. Solvothermal synthesis of CN based materials in several hot-mediators (DMF, CCl_4 , triethylamine, benzene, etc.) have been reported, and CN with various structure and morphology could be easily obtained [22–25]. Although the understand of microstructure especially the potential catalytic properties for these products is inadequate, the feasibility for synthesis of $g\text{-C}_3\text{N}_4$ material through hot-liquid mediated process is proved. Also, it is possible to design and modify the molecular stacking structure of $g\text{-C}_3\text{N}_4$ in order to improve the properties in catalytic/photocatalytic field.

In our previous work, wide visible-light responded $g\text{-C}_3\text{N}_4$ nanorod or hollow sphere was successful obtained from solvothermal method without template at 180°C . Under visible light irradiation, the products could obviously photocatalytic splitting of water to generate hydrogen ($6.1\ \mu\text{mol h}^{-1}$) or decomposition of organic pollutants to small molecules [26,27]. The group of Xu also obtained $g\text{-C}_3\text{N}_4$ sphere through this similar method at 200°C , but performed none H_2 evolution activity without post-treated by calcination [28]. For all this, the photocatalytic activity for $g\text{-C}_3\text{N}_4$ synthesized from low-temperature solvothermal route needs to improved.

In this work, O doped $g\text{-C}_3\text{N}_4$ hollow spheres were first synthesized from acetonitrile solvothermal method at 180°C . The effect of condensation time to the microstructure and morphology of products was investigated. Various activity tests, like photocatalytic decomposing of dyes, reduction of poisonous metal ions Cr(VI) and producing H_2 from water were carried out to evaluate the photocatalytic properties of obtained serious $g\text{-C}_3\text{N}_4$ hollow sphere.

2. Experimental

2.1. Preparation of catalysts

Graphitic carbon nitride hollow microsphere (CNO): The CNO was synthesis by solvothermal synthesis. Typically, 15 mmol cyanuric chloride (CC) and 11 mmol dicyandiamide (DCDA) powders were dispersed in 60 mL acetonitrile. The mixture was stirred for 12 h in a 100 mL Teflon-lined autoclave, and then the autoclave was sealed and maintained at 180°C for 12–96 h. The obtained products were sequentially washed with distilled water and absolute ethanol several times. After drying at 60°C for 12 h, products were obtained and defined as CNO-X, where X refers to the condensation time (h).

Pristine $g\text{-C}_3\text{N}_4$ (CNh) was prepared from direct calcination of dicyandiamide at 550°C for 2 h in air.

2.2. Catalyst characterization

The products were characterized by X-ray diffraction (XRD, D8 Advance) with Cu K α radiation. The morphology of the samples was explored using a JSM-7001F field-emission scanning electron

microscope (FE-SEM) and JEM-2010 high resolution transmission electron microscope (HR-TEM). Fourier transform infrared spectroscopy (FTIR) was recorded from KBr pellets in the range of $400\text{--}4000\ \text{cm}^{-1}$ on a Nicolet-360 FTIR spectrometer. X-ray photoelectron spectroscopy (XPS) analysis was performed on the ESCALAB 250 photoelectron spectrometer (ThermoFisher Scientific) with Al K α (1486.6 eV) as the X-ray source set at 100 W and a pass energy of 30 eV for high-resolution scan. UV-vis diffuse reflectance spectra (DRS) were measured With Lambda 750 UV/Vis/NIR spectrophotometer (Perkin-Elmer, USA) using BaSO_4 as reference. Photoluminescence (PL) spectra were accomplished in solid with Shimadzu RF5301 Spectrofluorophotometer with an excitation wavelength of 413 nm. The solid-state ^{13}C NMR experiment was performed on a Bruker AVANCE III 400 spectrometer.

2.3. Electrochemical analysis

Electrochemical measurements were conducted on a CHI 660E electrochemical workstation with a standard three-electrode cell. An FTO electrode deposited with samples, a platinum wire and saturated Ag/AgCl were employed as the working electrode, counter electrode and reference electrode, respectively. The working electrodes were prepared by drop coating method. The photocurrent and EIS were performed in 0.1 M Na_2SO_4 .

2.4. Measurement of photocatalytic activity

Photocatalytic properties of the products were tested in the decomposition of organic pollutant methyl orange (MO, 10 mg/L), reduction of aqueous Cr(VI) ($\text{K}_2\text{Cr}_2\text{O}_7$ aqueous solution, 25 mg/L) and hydrogen production. A 300 W Xeon lamp was used as exciting source. Without indication, the photocatalytic reactions were carryout out under visible-light ($\lambda > 420\ \text{nm}$).

Before illumination, 100 mL of MO and Cr(VI) with the addition of 50 mg catalyst was magnetically stirred for 30 min in dark to ensure the adsorption-desorption equilibrium. During illumination, about 4 mL of suspension was taken from the reactor at a scheduled interval. The concentration of MO was determined by absorbance analyse at 464 nm and the contents of Cr(VI) were determined using the diphenylacrbazide colorimetric method at 540 nm.

The photocatalytic H_2 production was carried out in a Pyrex top-irradiation reaction vessel connected to a glass closed gas system. 50 mg of catalyst power was dispersed in 100 mL aqueous solution containing 10 vol% triethanolamine as sacrificial electron donor. 3 wt% Pt was loaded on the surface of the catalyst by in situ photodeposition method using H_2PtCl_6 as co-catalyst. Before irradiation, the system was evacuated several times to remove air completely. The temperature of the reaction solution was maintained at 6°C by the flow of cooling water. The evolved gases were analyzed by gas chromatography equipped with a thermal conductive detector (TCD), using nitrogen as the carrier gas.

3. Results and discussions

3.1. Structural characterization of CNO samples

Fig. 1a presents the XRD patterns of as-prepared CNO catalysts. All materials show an obvious resembled typical $g\text{-C}_3\text{N}_4$ layered structure at 27.4° ($d = 0.326\ \text{nm}$) without an impurity phase. This distinct diffraction peak belongs to the long-range inter planar stacking of aromatic systems identified as the (002) peak. Impressively, the intensity of the main (002) peak gradually decreased with the extended condensation time, indicating decreased long-range order of graphitic stacking. Compared to typical graphite XRD pattern of CN material, the peak at $\sim 13^\circ$ as the (100) peak is not

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