



# Construction of novel three dimensionally ordered macroporous carbon nitride for highly efficient photocatalytic activity



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## ABSTRACT

The construction of multi-porous nanostructured  $g\text{-C}_3\text{N}_4$  photocatalyst is an efficient strategy to separate charge carriers and enhance the photocatalytic activity in the visible light region. Here we utilized a simply thermal condensation-assisted colloidal crystal template method to construct the novel and highly efficient three dimensionally ordered macroporous (3DOM)  $g\text{-C}_3\text{N}_4$  photocatalyst for the photocatalytic oxidation of pollutants. The effects of microstructure, crystallinity, textural properties and optical absorption ability on the photocatalytic activity of 3DOM  $g\text{-C}_3\text{N}_4$  have been systematically probed. Characterization and photocatalytic test results showed that the 3DOM architecture has the unique structure sensitive property to light trapping, reactant transfer and photoreaction, and this property leads 3DOM  $g\text{-C}_3\text{N}_4$  to produce a narrowed electronic band gap (2.65 eV) and own superior photocatalytic performance for the degradation of organic dye. Compared to pure  $g\text{-C}_3\text{N}_4$  (lamellar structure), 3DOM  $g\text{-C}_3\text{N}_4$  shows approximately 5.3 times higher catalytic activity. A possible mechanism of the photoactivity enhancement was proposed based on the photocurrent measurement, photoluminescence analysis and the quenching experiments. This work highlights that the construction of 3DOM architecture could provide a useful strategy to design and fabricate highly efficient  $g\text{-C}_3\text{N}_4$  photocatalysts.

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## 1. Introduction

The construction of three dimensionally ordered macroporous (3DOM) architecture has been one of the most attractive options to improve the performances and extend the applications of semiconductor materials [1–4]. It has been known that the materials with 3DOM architecture not only possess uniformly distributed macroporous structure and high porosity [5–7], but also own strong photon trapping capacity and electron transport ability [8,9], and these above structure characteristics for the 3DOM semiconductors can be acted as the optical absorption active sites, which can facilitate the light trapping and charge separation and migration. Besides the unique optoelectronic properties, the most attractive feature of the 3DOM materials is their special structure sensitive property for catalytic reaction, because this kind of advanced architecture with an open, interconnected macroporous network could supply a large number of surface defects, step positions and atom vacancies on their inside and outside surfaces, and these unique spots

can serve as “interfacial chemical reaction active sites” to enhance the absorption, mass diffusion and removal of reactant during the photocatalytic reaction. Owing to the co-existence of optical absorption active sites and interfacial reaction active sites, the 3DOM materials have shown extremely high use-value in various applications, particular in the solar energy conversion and environmental protection. Till date, various 3DOM photocatalytic materials have been successfully synthesized through the colloidal crystal template method, including 3DOM  $\text{N-TiO}_2$  [8], 3DOM  $\text{InVO}_4\text{-BiVO}_4$  [9], 3DOM  $\text{Pr}_6\text{O}_{11}$ , 3DOM  $\text{Tb}_4\text{O}_7$  [10], 3DOM  $\text{Co}_3\text{O}_4$  [11], etc. All the above-mentioned 3DOM materials show more efficient visible light utilization and improved photocatalytic activity.

Recently, as a new form of metal-free organic semiconductor material, graphitic carbon nitride ( $g\text{-C}_3\text{N}_4$ ) has become a hotspot in the field of photocatalysis. This material possesses outstanding optical and electronic properties, remarkable thermal and chemical stability, easily adjustable band structure, low cost and facilely synthetic process [12–14]. However, the traditional two-dimensional lamellar  $g\text{-C}_3\text{N}_4$  has some prominent disadvantages, such as the relatively narrow visible light responsive region, poor quantum efficiency caused by the high recombination probability of photogenerated electron-hole pairs and the low specific surface area. To overcome the inherent disadvantages of  $g\text{-C}_3\text{N}_4$ , a large num-

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ber of strategies have been developed, for instance by doping with nonmetallic elements to harvest a wider portion of solar light [15], by coupling with a narrow matched band gap semiconductor to promote the effective separation of photogenerated charges [16] and by constructing porous nanostructures to increase the photocatalytic reactive surface area [17]. In recent years, preparation of  $g\text{-C}_3\text{N}_4$  with porous nanostructures, especially with 3DOM structure, has been considered to be a promising way to obtain a high-performance visible-light-induced  $g\text{-C}_3\text{N}_4$  photocatalyst. As is well known, compared with the two-dimensional lamellar  $g\text{-C}_3\text{N}_4$ , the 3DOM  $g\text{-C}_3\text{N}_4$  with periodic macroporous structure not only can produce numerous access channels for the mobility of photogenerated carriers and the transfer of reactant species, but also can increase the visible light absorption efficiency induced by multiple scattering and slow photon [3,8]. To date, however, it is still extremely challenging to seek an efficient synthetic approach for 3DOM  $g\text{-C}_3\text{N}_4$  photocatalyst. Because the common  $g\text{-C}_3\text{N}_4$  grain with large sheet-like structure is extremely hard to be wrapped and immersed into the interstices of the templates, so that the formation process of three dimensionally ordered macroporous architecture for  $g\text{-C}_3\text{N}_4$  is quite difficult to achieve under this situation. Until now, to the best of our knowledge, there is few work on studying the 3DOM  $g\text{-C}_3\text{N}_4$ , except the 3DOM  $g\text{-C}_3\text{N}_4/\text{C}$  composite very recently reported by Liang et al. [18], which prepared through coupling  $g\text{-C}_3\text{N}_4$  on the framework of 3DOM carbon material.

In this paper, the novel  $g\text{-C}_3\text{N}_4$  with three dimensionally ordered macroporous architecture was firstly constructed via a thermal condensation-assisted colloidal crystal template method. It is worth noting that the construction of 3D ordered mesoporous core-shell  $\text{SiO}_2$  template is the key step for guaranteeing the successful preparation of 3DOM  $g\text{-C}_3\text{N}_4$ , because this special template can effectively prompt the precursor to fill into the voids in the mesoporous  $\text{SiO}_2$  shell and prevent the loss of active ingredients during calcination process. The microstructure, crystal phase, textural properties and optical absorption ability of the obtained photocatalysts were studied by a variety of techniques, and the promising application value of 3DOM  $g\text{-C}_3\text{N}_4$  was evaluated by the photodegradation of rhodamine B (RhB) under visible-light ( $\lambda \geq 420 \text{ nm}$ ) illumination. On basis of the characterization and photocatalytic results, the relationship between 3DOM structure and photoactivity of  $g\text{-C}_3\text{N}_4$  was proposed.

## 2. Experimental

### 2.1. Material synthesis

All reagents for synthesis and analysis were commercially available and used without further treatment.

#### 2.1.1. Synthesis of 3D ordered mesoporous core-shell $\text{SiO}_2$ nanospheres

The solid  $\text{SiO}_2$  core was prepared according to our previously reported method [19]. Typically, 10 mL of tetraethyl orthosilicate (TEOS) was dispersed in 50 mL of ethanol with vigorous stirring to form solution A, meanwhile, 10 mL of aqueous ammonia and 20 mL of deionized water were added to 50 mL of ethanol with vigorous stirring to form solution B. The solution A and solution B were mixed, constantly stirred and heated at  $40^\circ\text{C}$  for 2.5 h to obtain the uniform  $\text{SiO}_2$  nanospheres (solid  $\text{SiO}_2$  core). Then a mixture solution of certain amount of TEOS, polyvinylpyrrolidone (PVP) K30 ( $M_w \sim 40\,000$ ) and ethanol was added dropwise to the above silica sol with vigorous stirring at  $40^\circ\text{C}$  for 2 h to form the  $\text{SiO}_2$  shell covered on the surface of solid  $\text{SiO}_2$  core. And after standing at room temperature overnight, the mixed solution was centrifuged to construct the ordered structure, and then dried at  $60^\circ\text{C}$  in a

vacuum drying oven for 12 h. The dried ordered  $\text{SiO}_2$  template was calcinated at  $700^\circ\text{C}$  for 6 h in air to remove PVP and obtain the mesoporous shell. The final 3D ordered mesoporous core-shell  $\text{SiO}_2$  nanospheres with the average diameter of 280–340 nm were obtained following this way.

#### 2.1.2. Synthesis of 3DOM $g\text{-C}_3\text{N}_4$

Certain amount of 3D ordered mesoporous core-shell  $\text{SiO}_2$  template was treated with 10 mL of 1 M HCl solution, then dried in a drying oven at  $60^\circ\text{C}$  for 12 h. The treated  $\text{SiO}_2$  template was impregnated into 2 g of melted cyanamide liquid at  $60^\circ\text{C}$  for 12 h. Then the mixture was vigorously stirred at  $60^\circ\text{C}$  for 6 h and dried in water bath at  $80^\circ\text{C}$  to obtain white solid. Next, the mixture was calcined at  $550^\circ\text{C}$  for 4 h in a tube furnace with a heating ramp of  $2.3^\circ\text{C min}^{-1}$  in nitrogen atmosphere. Finally, the 3DOM  $g\text{-C}_3\text{N}_4$  was obtained by removing the 3D ordered mesoporous core-shell  $\text{SiO}_2$  template with hydrofluoric acid.

#### 2.1.3. Synthesis of pure $g\text{-C}_3\text{N}_4$

2 g cyanamide was directly calcined at  $550^\circ\text{C}$  for 4 h in a tube furnace with a heating ramp of  $2.3^\circ\text{C min}^{-1}$  in nitrogen atmosphere, the resultant canary yellow powder was collected for using as a reference.

## 2.2. Characterization

The crystal structures of all as-prepared photocatalysts were detected by X-ray diffraction (XRD; SHIMADZU, Lab X XRD-6000). The microstructures and morphologies of all samples were examined by transmission electron microscopy (JEOL, JEM-2100) and scanning electron microscopy (JEOL, JSM-6700F, 200 kV). UV–vis diffuse reflectance spectra (DRS) were recorded on a Hitachi U-4100 UV–vis spectrometer using  $\text{BaSO}_4$  as the reference. Fourier transform infrared (FT-IR) spectra were conducted on a Nicolet Avatar 360 FT-IR instrument. The textural properties of photocatalysts were investigated using a BET analyzer (ASAP 3000), and specific surface area and pore size distribution of the samples were obtained by the Brunauer-Emmett-Teller (BET) equation and Barrett-Joyner-Halenda (BJH) method, respectively.  $\text{CO}_2$  temperature-programmed desorption ( $\text{CO}_2\text{-TPD}$ ) tests were performed on a ChemBET Pulsar TPR/TPD apparatus (Quantachrome, U.S.A.) over a temperature range of  $60\text{--}380^\circ\text{C}$  at a ramp rate of  $10^\circ\text{C min}^{-1}$  in helium atmosphere. The photoluminescence (PL) emission spectra were measured using a HORIBA JY Fluorolog-3 type fluorescence spectrophotometer with an excitation wavelength of 340 nm.

## 2.3. Adsorption measurement

The adsorption experiments were executed to investigate the adsorption performances of the samples. Briefly, 0.07 g of the as-prepared photocatalysts were added into 70 mL of Rhodamine B (RhB,  $10 \text{ mg L}^{-1}$ ) aqueous solution and stirred in the dark. Every 5 min, 3 mL of the solution was collected and centrifuged to isolate the photocatalyst powder, and the concentration of filtrated RhB solution was analyzed by a UV–vis spectrophotometer (UV-1900PPC, Shanghai, China) at the maximum characteristic wavelength of 554 nm.

The capacity of the photocatalysts to adsorb RhB molecules can be calculated by the following formula:

$$Q_t = \frac{C_0 - C_t}{M} \times V \quad (1)$$

where  $Q_t$  ( $\text{mg g}^{-1}$ ) represents the instantaneous amount of adsorbed RhB on per gram of the photocatalyst (at time  $t$ ),  $C_0$  and  $C_t$  represent the initial and instantaneous (at time  $t$ ) concentration of

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