



Influence of solvothermal synthesis on the photocatalytic degradation activity of carbon nitride under visible light irradiation



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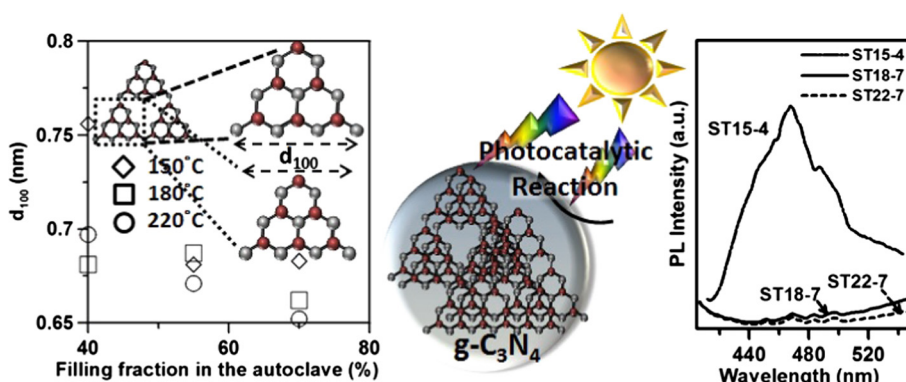
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HIGHLIGHTS

- $g\text{-C}_3\text{N}_4$ is solvothermally prepared with different conditions of the autoclave.
- A phase transition of $g\text{-C}_3\text{N}_4$ is observed in the solvothermal synthesis.
- Contraction of d_{100} spacing of $g\text{-C}_3\text{N}_4$ leads to the reduced PL emission.
- High photocatalytic activity to degrade methylene orange dye is obtained.

GRAPHICAL ABSTRACT

Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) has been synthesized using a solvothermal method, revealing an excellent photocatalytic degradation activity under visible light illumination.



ARTICLE INFO

Article history:

Received 16 December 2016
 Received in revised form 10 March 2017
 Accepted 23 March 2017
 Available online 27 March 2017

Keywords:

Graphitic- C_3N_4
 Photocatalyst
 Visible light
 Solvothermal method

ABSTRACT

The demand for the development of metal-free, visible-light-active photocatalysts is increasing. This study reports the solvothermal synthesis of carbon nitride (C_3N_4) photocatalysts by using acetonitrile as a solvent and solvothermal temperatures of 150–220 °C. The crystalline structures of the resulting C_3N_4 samples were obtained following a conversion from a mixed pseudocubic/beta phase to a graphitic phase by increasing the solvothermal temperature and the filling fraction of the autoclave. The interlayer spacing of tri-*s*-triazine units in the (100) direction within graphitic C_3N_4 ($g\text{-C}_3\text{N}_4$) was obtained from X-ray diffraction measurements and was observed to decrease because of pressurization, leading to improved interlayer stacking of the tri-*s*-triazine units and a high degree of overlap between the *n* states and antibonding π orbitals. The prepared catalysts had band gap energies of 1.5–2.5 eV, and the $g\text{-C}_3\text{N}_4$ samples had high photocatalytic activity during the degradation of methyl orange solutions under visible light irradiation. The $g\text{-C}_3\text{N}_4$ samples obtained at high temperatures and filling fractions exhibited lower photoluminescence emission intensities than did the C_3N_4 specimens with mixed phases (i.e., pseudocubic- and beta- C_3N_4), suggesting that these active $g\text{-C}_3\text{N}_4$ catalysts with compact planar tri-*s*-triazine units had efficient charge separation. The present study demonstrated the influence of the experimental conditions used in the synthesis of C_3N_4 on the subsequent photocatalytic degradation activity of the specimens under visible light irradiation.

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1. Introduction

Since the theoretical prediction of beta-C₃N₄ by Liu and Cohen (1989), numerous reports have described both theoretical and experimental research on three-dimensional carbon nitrides, such as alpha-C₃N₄ (α -C₃N₄), beta-C₃N₄ (β -C₃N₄), cubic-C₃N₄ (c-C₃N₄), and pseudocubic-C₃N₄ (pc-C₃N₄), and the two-dimensional graphitic-C₃N₄ (g-C₃N₄) (Ong et al., 2016; Thomas et al., 2008; Dong et al., 2014b; Zhang et al., 2016). In recent years, more attention has been focused on their potential applications, such as photocatalytic water splitting (Butchosa et al., 2014; Srinivasu et al., 2014; Martin et al., 2014; Chen et al., 2015; Indra et al., 2017; Zheng et al., 2016); CO₂ capture and reduction (Oh et al., 2015; Lin et al., 2014; Kuriki et al., 2015); photodegradation of pollutants and wastewater treatment (Dong et al., 2014a; Rong et al., 2015); and in transesterification (Xu et al., 2015), hydrogenation, and oxidation reactions (Gong et al., 2015; Yuan et al., 2015; Arrigo et al., 2016; Wang et al., 2008). Wang et al. successfully synthesized g-C₃N₄ by heating cyanamide at 673–873 K and used it as a photocatalyst for water splitting and the photodegradation of organic pollutants under visible light irradiation, beginning a new line of research on the photocatalytic performance of g-C₃N₄.

Different C₃N₄ crystalline structures have been prepared and predicted in the last few decades. Although α -C₃N₄ has a tetrahedral structure and C–N interconnections through sp³ hybridization (Wang and Jiang, 2014), β -C₃N₄, with hexagonal packing of sp³-bonded carbon and trigonal planar sp²-bonded nitrogen atoms, has a structure containing 14 atoms per unit cell that is identical to that of β -Si₃N₄ (Fig. 1a) (Yin et al., 2003a, 2003c). However, it is difficult to synthesize β -C₃N₄ because of its low thermodynamic stability (Nesting and Badding, 1996). g-C₃N₄ is generally prepared using thermal condensation and has a graphitic feature with tri-s-triazine units (C₆N₇) and stacking of the conjugated aromatic system (Wang et al., 2008). Kroke et al. (2002) reported that the tri-s-triazine tectonic units in g-C₃N₄ are relatively stable because of the electronic environment provided by N atoms and the size of the nitride pores (Fig. 1b). Fig. 1c illustrates the defected zinc-blende-like structure of pc-C₃N₄ (space group $P\bar{4}3m$), which is identical to that of β -C₃N₄ (Liu and Wentzcovitch, 1994).

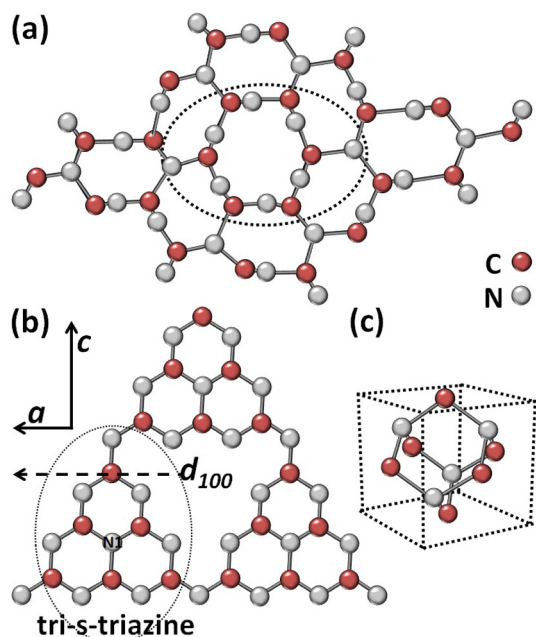


Fig. 1. Schema of atomic structures of (a) β -C₃N₄, (b) g-C₃N₄, and (c) pc-C₃N₄.

Many attempts have recently been made to prepare carbon nitrides by using different previously reported methods, including physical and chemical vapor deposition (Zhang et al., 1999) and high temperature and high pressure processes (Montigaud et al., 2000). The synthesis of C₃N₄ by using a solvothermal method has also been reported, and this method demonstrated low energy consumption, uniform and fine particle formation, controllable morphology, and cost effectiveness compared with traditional thermal condensation methods (Bai et al., 2003; Zhang et al., 2013a; Cui et al., 2012; Sano et al., 2013). An alkaline hydrothermal treatment at 90–150 °C was previously used for a g-C₃N₄ photocatalyst to remove the unstable domains of the poorly ordered carbon nitride, leading to the formation of a mesoporous structure with a surface area of 65 m² g⁻¹ (Sano et al., 2013). Guo et al. successfully prepared g-C₃N₄ through a solvothermal process by using cyanuric chloride and sodium amide in benzene at 200 °C for 8–12 h (Guo et al., 2003). Furthermore, g-C₃N₄ nanotubes and nanobelts with diverse morphologies were synthesized solvothermally by Li and coworkers by using dicyandiamide or melamine in CCl₄ at 290 °C and at 4.5–5 MPa for 24 h (Li et al., 2007). Although extensive studies on the various syntheses and characterizations of carbon nitride materials have been reported, the effect of the solvothermal experimental conditions (i.e., temperature and filling fraction) on the crystalline structures and photocatalytic activity of carbon nitride materials has rarely been considered. Because solvothermal methods are simple to use, they deserve in-depth investigation.

A detailed examination of the structure of C₃N₄ materials synthesized using a solvothermal method is essential to elucidate the structural transformation of C₃N₄ under different conditions. Therefore, this study investigated in detail the crystalline structure of C₃N₄ specimens formed by solvothermal synthesis and their photoluminescence and photocatalytic performance during methyl orange degradation upon illumination with visible light.

2. Experimental

In this study, solvothermal synthesis was performed to prepare C₃N₄ powders. Cyanuric chloride (C₃N₃Cl₃; Alfa Aesar, 99.9%) and sodium azide (NaN₃; Alfa Aesar, 99.9%) were solvothermally treated using acetonitrile (CH₃CN; Alfa Aesar, 95%) as a solvent in 100 mL of Teflon-lined autoclave at 150, 180, and 220 °C for 15 h. The filling fractions of the solution in the autoclave were 40%, 55%, and 70% to determine the essential crystal growth of carbon nitride samples. After the solvothermal treatment, slurries were washed with distilled water and ethyl alcohol several times. The obtained products were centrifuged and then dried at 80 °C for 6 h to yield the final powders. The characteristics of these powders are summarized in Table 1. The samples were designated as ST15-4, ST15-5, ST15-7, ST18-4, and ST22-7, where ST stands for “solvothermal”; 15, 18, and 22 indicate a solvothermal temperature of 150, 180, and 220 °C, respectively; and 4, 5, and 7 denote a filling fraction of 40%, 55%, and 70%, respectively.

The crystalline structure of the C₃N₄ specimens was identified by using X-ray diffraction (XRD; D8 advance, Bruker, USA). The XRD patterns were collected at 2 θ angles of 5–60° at 40 kV, 40 mA, and a scan rate of 4° min⁻¹. The microstructures of the products were investigated through scanning electron microscopy (SEM; S-4800N, Hitachi, Japan). Elemental composition was determined using energy dispersive X-ray spectroscopy (EDS) coupled to the SEM. To characterize the chemical structure of the samples, the C₃N₄ powders were mixed with KBr and ground thoroughly and then pressed into a pellet and analyzed using Fourier transform infrared spectroscopy (FTIR; Tensor 27, Bruker, USA). The electron binding energy of the samples was determined through

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