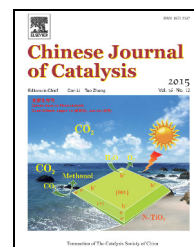


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Communication (Special Issue on Photocatalysis)

Thermal nitridation of triazine motifs to heptazine-based carbon nitride frameworks for use in visible light photocatalysis



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ARTICLE INFO

Article history:

Received 6 September 2015

Accepted 14 October 2015

Published 20 December 2015

Keywords:

Carbon nitride

Thermal nitridation

Polymerization

Photocatalysis

Hydrogen evolution

ABSTRACT

A thermal nitridation route for the assembly and polymerization of molecular triazine units to heptazine-based covalent frameworks has been successfully established. The obtained conjugated carbon nitride polymers feature nanostructures that show enhanced photocatalytic reactivity for hydrogen production under visible light irradiation.

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Nitride-based solid-state materials have attracted a great deal of attention in many fields. For example, numerous studies have focused on the use of multifarious metal and non-metal nitrides as semiconductor photocatalysts to achieve efficient photon energy conversion [1,2]. The reported studies have clearly shown that the valence band of nitride semiconductors commonly consists of N 2p orbitals or hybridized N 2p and O 2p orbitals (such as Ta₃N₅ and TaON) above the O 2p valence band of the corresponding oxides (e.g., Ta₂O₅). This serves to extend the photoactive region to the visible spectrum for efficient use of sunlight [3]. Therefore, many nitride semiconductors activated by visible light have been exploited and are considered as important candidates for artificial energy conversion, although the stability of these nitride-based inorganic semiconductors is a concern [4,5]. It is reported that surface kinetic controls using co-catalysts can significantly prevent metal nitride photocatalysts from photo-corrosion, increasing the potential of a num-

ber of nitride semiconductors for use in artificial photosynthesis.

The graphitic carbon nitride (CN) polymer is a semiconductor regarded as the most stable crystal phase of the binary CN allotropes under ambient conditions. Since the report of CN redox photocatalysis in 2009, this robust conjugated polymer, with a band gap of ~2.7 eV, has stimulated a great deal of scientific interest owing to its unique and tunable optical and electronic properties [6–8]. According to previous studies, CN polymers are usually synthesized by a bulk self-polymerization reaction of N-rich precursors at high temperature (500–650 °C) [9–11]. The starting materials are generally the compounds containing or engendering triazine motifs in these reactions. The bulk condensation is typically limited by reaction kinetics, and the synthetic materials are not well condensed/crystalline and exhibit low specific surface areas. It has been shown that the crystallinity of a semiconductor greatly influences its pho-

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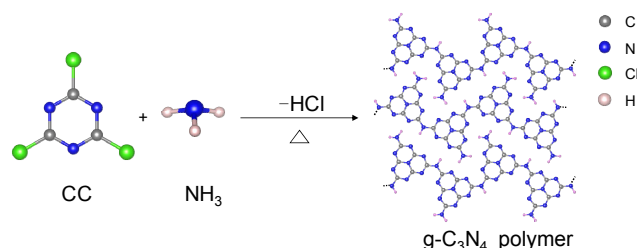
This work was supported by the National Basic Research Program of China (973 Program, 2013CB632405), the National Natural Science Foundation of China (21425309, 21033003), the Specialized Research Fund for the Doctoral Program of Higher Education (20133514110003), and the Department of Education of Fujian Province in China.

DOI: 10.1016/S1872-2067(15)60995-0 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 36, No. 12, December 2015

toredox function because the crystal structure imperfections can hamper the fast migration and separation of light-induced charge carriers [12,13]. Recently, it has been shown that the crystallinity of the CN polymer can be observably enhanced by heating melamine in an airtight system under an autogenic pressure of NH_3 , compared with that of CN synthesized by pyrolyzing melamine in ambient air [14]. The enhancement in crystallinity stems from the condensation reactions. However, the materials thus produced in the closed system are generally triazine-based CN polymers with a much reduced photocatalytic activity. Therefore, a new synthetic procedure for carbon nitride polymers is called for.

It is well known that the nitrogen in NH_3 gas, generally a nucleophilic reagent, is very reactive at high temperature, reacting with metals or metal chlorides/oxides to produce metal nitrides/oxy-nitrides [15–17]. The nitrogen can also react with non-metal elements, such as B, P, or Si, to yield the corresponding non-metallic nitride materials [18,19]. Indeed, the synthesis of nitrogen-rich carbon-based materials has been demonstrated by thermal annealing of amorphous carbon powders under NH_3 atmosphere at high temperature ($> 1000^\circ\text{C}$), revealing that the nitrogen can combine with the stable carbon structure to form covalent C–N bonds at high temperature [20]. However, the nitridation of organic molecules with NH_3 at high temperature, to produce nitride semiconductors for heterogeneous photocatalysis, has not been widely reported, and thus far, the nitridation of triazine trichloride by the acid-base polymerization reaction to form covalent carbon nitride frameworks is yet to be investigated.

Herein, we introduce a thermal nitridation route for the synthesis of well-defined heptazine-based covalent carbon nitride frameworks by using NH_3 and solid triazine trichloride as starting materials, and explore their photocatalytic reactivities. Our experiments show that the synthetic route allows one to nitridize the solid cyanuric trichloride into heptazine-based CN nanostructures at elevated temperature, as shown in Scheme 1. In the first stage of the synthesis, the gas-phase nitridation of organic molecules can produce a carbon nitride polymer composed of *s*-triazine rings from a nucleophilic substitution reaction of solid triazine trichloride with NH_3 . Chlorine can easily depart from the triazine trichloride to produce NH_4Cl after the reaction of the formed HCl with NH_3 , and the amino group is strongly bound with carbon because the amino group is a much poorer leaving-group than chlorine [21]. Polymeric CN materials consisting of triazine motifs are kinetically labile with regard to their further conversion into hep-



Scheme 1. Thermal nitridation induced polymerization of cyanuric trichloride (CC) to $\text{g-C}_3\text{N}_4$ with flowing NH_3 .

tazine-based carbon nitride frameworks at high temperature [22]. This nitridation process might yield well-condensed polymelon by fusion of triazine units.

In our experiments, thermal-nitridation-derived carbon nitride samples were synthesized by heating cyanuric chloride (1.38 g) at a certain temperature for 2 h with a ramp rate of $5.0^\circ\text{C}/\text{min}$ under flowing NH_3 (25 mL/min). The as-synthesized products are denoted as CNC-*X*, where *X* is an arbitrary number that represents the pyrolyzing temperature (Table 1). As a reference, melamine-derived carbon nitride (g-CN), synthesized from the traditional thermal-condensation process, was also obtained [9]. We then investigated the properties of well-defined carbon nitride polymers prepared at different degrees of layer condensation, and studied the visible light-activated catalytic performance of the resultant CNC samples for hydrogen photosynthesis from an aqueous solution of triethanolamine.

First, we analyzed the chemical structure and composition of the products by X-ray photoelectron spectroscopy (XPS) characterization, which is sensitive to the chemical environment of lightweight elements. Signals of C, N, and O in the survey spectrum in Fig. 1(a) were recorded, but no peak assigned to Cl could be observed. The absence of Cl in the final sample was confirmed by the high-resolution spectra of Cl 2*p*, as shown in Fig. 1(b). The absence of Cl species in the as-prepared CNC solid is further confirmed by elemental analysis, and the values of the C/N ratios are in accordance with that of the melamine-derived g-CN (Table 1). Additionally, the presence of O is probably the result of the H_2O and O_2 adsorbed on the surface of the resulting samples. The structure details relating to the framework C and N elements in the CNC-3 sample were measured by their corresponding high-resolution spectra. The C 1*s* XPS spectrum in Fig. 1(c) shows one main peak at 287.9 eV, which is related to an sp^2 -bonded carbon (N–C=N). The other weak C 1*s* peak at 284.6 eV is attributed to carbon impurities [10]. In Fig. 1(d), the N 1*s* spectrum can be deconvoluted into four peaks. The strongest N1*s* peak at 398.4 eV is identified as an sp^2 -bonded nitrogen (C–N=C). The N 1*s* peaks at 399.5 and 400.7 eV are attributed to N atoms that are bound to three C atoms. The last peak at 404.1 eV is assigned to π -excitations. This result reveals that the as-obtained CNC-3 sample is dominated by tri-*s*-triazine structures that are basic units of the g-CN polymer, as confirmed by the solid-state ^{13}C nuclear magnetic resonance (NMR) analysis (Fig. 2), in which there are two groups of resonances at $\delta = 162.5/164.8$ and 156.4, separately assigned to $\text{CN}_2(\text{NH}_x)$ and CN_3 motifs [14].

The X-ray diffraction (XRD) patterns of CNC materials are

Table 1
Physicochemical properties of g-CN and CNC samples.

Catalyst	A_{BET} (m^2/g)	C/N molar ratio	H content (wt%)	HER ^a ($\mu\text{mol}/\text{h}$)
g-CN ^b	10	0.67	1.91	12
CNC-1 ^c	26	0.66	2.04	68
CNC-2 ^c	54	0.67	1.76	101
CNC-3 ^c	69	0.68	1.61	120

^a H_2 evolution rate.

^b Synthesized by heating melamine at 550°C in air.

^c The numbers 1, 2, and 3 correspond to reaction temperatures of 500, 550, and 600°C , respectively.

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