Microporous and Mesoporous Materials 211 (2015) 182–191

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Synthesis and comparative study of the photocatalytic performance of hierarchically porous polymeric carbon nitrides

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ARTICLE INFO

Article history:
Received 24 November 2014
Received in revised form
24 February 2015
Accepted 25 February 2015
Available online 13 March 2015

Keywords:
Carbon nitride
H_2 evolution
Photocatalytic degradation
Crystallinity
Texture

ABSTRACT

Graphitic carbon nitride materials with tri-*s*-triazine and *s*-triazine based structures were prepared by thermal condensation of melamine (CNT) and by solution reaction of cyanuric chloride with lithium nitride (CNS), respectively. An amphiphilic block copolymer-F68 was used as a soft template for the synthesis of mesoporous carbon nitride. The structural and photophysical properties of the as-prepared catalysts were characterized by X-ray powder diffraction, elemental analysis, N_2-adsorption measurement, transmission electron microscopy, X-ray photoelectron spectroscopy, differential scanning calorimeter and UV–Vis absorption as well as time-resolved picosecond emission spectroscopy. The photocatalytic activity of the samples was evaluated by H_2 evolution from water under visible light irradiation and the degradation of rose bengal (RB). The mesoporous CNT materials prepared with Pluronic F68 as template showed markedly higher activity compared to bulk carbon nitride, which can be attributed to its crystallinity, hierarchical porous structure and the enlarged surface area. The catalyst was relatively stable as proven by recycling experiments. Besides, the addition of H_2O_2 promoted the formation of active ·OH radicals and increased the activity of carbon nitride for photodegradation of rose bengal. The carbon nitrides prepared by solution reactions were of very poor activity both in photocatalytic water splitting and rose bengal degradation.

1. Introduction

Photocatalysis is a green, economical and efficient technology to use light, ideally solar light, to drive catalytic reactions, which has wide application in water/air purification, hydrogen production from water and energy conversion [1]. Many inorganic semiconductors have been used as photocatalyst in the degradation of environmental hazardous organic pollutants and hydrogen evolution from water, including titania-based system, metal oxides, metal sulfides, and nitrides and others [2–7]. Most active catalysts work with UV light. Recently, a very active ZnS/Fe quantum dot system has been reported [8]. The extension of the used spectral range of sunlight into the visible range to increase the energetic efficiency by using lower band gap materials is a challenge.

Graphitic carbon nitride (g-C_3N_4) is a polymer semiconductor with a moderate band gap of *ca.* 2.7 eV, showing an intrinsic semiconductor-like absorption in the blue region of the visible spectrum. It has a high thermal and chemical stability [9,10]. Carbon nitrides (CNs) with different composition (C/N ratio) and morphology have been synthesized by different methods and precursors [9–12]. Bulk CNs have been modified by using templates, blending dopants, and copolymerization to improve their porosity and surface areas [13–16]. Mesoporous g-C_3N_4 has been prepared by thermal polymerization of different nitrogen-rich precursors using hard templates (silica) and soft templates (e.g. the poly(ethylene glycol)-poly(propylene glycol) triblock

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http://dx.doi.org/10.1016/j.micromeso.2015.02.050
1387-1811/

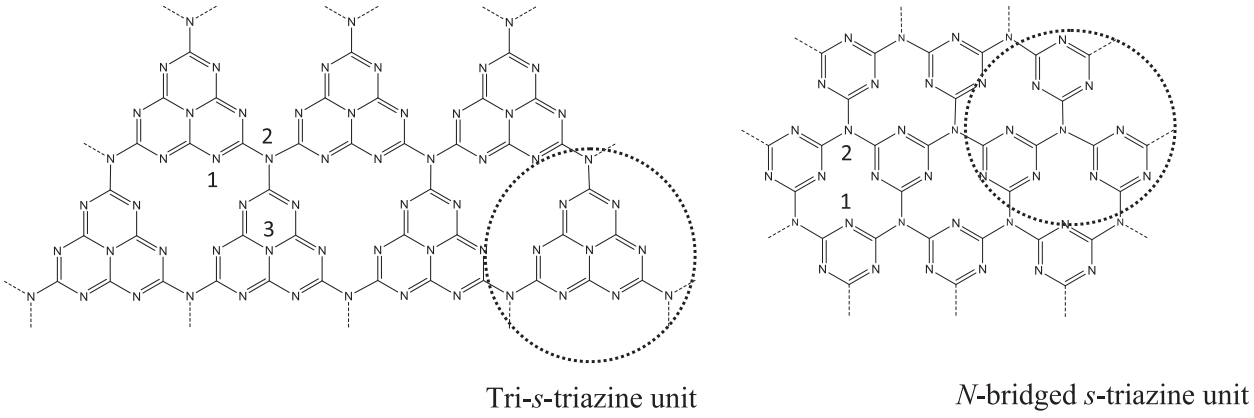

Fig. 1. Structure scheme of g-C_3N_4 with N-bridged tri-s-triazine and s-triazine as building blocks.

copolymer P123, the surfactant Triton X-100, a poly(ethylene oxide) chain with aa alkyl aromatic head group, and some ionic liquids) [17–19]. Vinu et al. reported the synthesis of mesoporous carbon nitride by chemical synthesis with ethylenediamine and carbon tetrachloride using the ordered mesoporous silica SBA-15 as hard template [20]. The obtained CN materials featured high surface areas and well-ordered porous structures. But the C/N ratio was very high (*ca.* 5) and the crystallinity was low. By controlling the condensation temperature of the precursor (dicyanodiamide) nitrogen-deficient g-C_3N_4 was obtained [21].

It is well-known that the synthesis method and precursors have great effect on the resulting structure, composition, electronic properties, and the photocatalytic performance. The g-C_3N_4 materials studied in recent years were mostly prepared by thermal condensation of cyanamide or melamine displaying a network of *N*-bridged tri-*s*-triazine units (Fig. 1), which turned to be a hot choice for photocatalysis [9,10]. Wang and Antonietti et al. found that g-C_3N_4 could produce hydrogen from water under visible-light irradiation in the presence of a sacrificial donor [11,15–17]. Furthermore, Yan et al. reported the photocatalytic performance of g-C_3N_4 in the degradation of organic dyes [12,13]. Another studies showed, that mesoporous g-C_3N_4 usually exhibited better photocatalytic performance than bulk, μm-sized g-C_3N_4 for several reactions such as hydrogen evolution from water, selective oxidation of alcohols, and removal of phenol [22,23]. It was suggested that the existence of nitrogen vacancies led to the improvement of the performance for photodecomposition of rhodamine B and photocatalytic hydrogen evolution [21].

Another modification of g-C_3N_4 with a network of *N*-bridged *s*-triazine units (Fig. 1) was prepared by different methods including a solvent-thermal route, solid-state reaction and low temperature solution reaction [24–26]. Usually, cyanuric chloride or fluoride was used as *s*-triazine building blocks, and Li_3N, K or $NaNH_2$ as a nitrogen-bridging reagent. But the properties of this modification of CNs have not been studied intensively so far, especially the influence of the textural properties on the photocatalytic properties of these materials compared to melamine-based materials.

In the present work, g-C_3N_4 and mesoporous g-C_3N_4 materials are prepared by two methods: (i) thermal condensation of melamine (CNT-1 materials) and (ii) solution reaction of cyanuric chloride with lithium nitride (CNS-1 materials). The former are based on tri-*s*-triazine units and the latter on *s*-triazine units. An amphiphilic block copolymer was used as soft template for the synthesis of the (meso)porous variants CNT-2 and CNS-2, respectively. Their physical and chemical properties were studied and compared in detail. The photocatalytic performances of these two g-C_3N_4 materials were tested in two model reactions: (i) the H_2 evolution from water and (ii) the degradation of rose bengal (RB). The performances of the mesoporous CNT material in photodegradation of RB under different conditions are surveyed in particular at comparatively low catalyst concentration and low irradiation intensity (60 W UV Vis solarium lamp).

Rose bengal (4,5,6,7-tetrachloro-2′,4′,5′,7'-tetraiodofluorescein) and its derivate are new emerging pollutants in surface and probably drinking water. It is a dye stain which can lead to severe health problems and detrimental effects on the aquatic species [27,28] which are hazardous even at low concentration. Rose bengal is increasingly used and released into the environment due to its application potential in different areas. It can be used in treatment of certain cancer and skin conditions as eczema and psoriasis. It is also widely used contrast agent in medical and biological diagnostics and is a potential candidate for molecular electronics [29,30].

Conventional water treatment processes like adsorption, coagulation, ultrafiltration, elimentation and the membrane process are not able to remove these contaminations completely without adding chemicals. Often they do not degrade the hazardous compound as could be shown by combined UV/H_2O_2 treatment [31,32]. Heterogeneous photocatalytic degradation using semiconductors is, therefore, an interesting option. The bleaching products of rose bengal bleaching under reducing condition was studied showing the formation of a couple of semi-oxidized intermediates [33]. Bismuth sulfide [34] and nanocrystalline and porous FeS thin films [35] have been used for rose bengal degradation. Operational parameter have been studied with zinc oxide [36] and photoelectrocatalytic oxidation of rose bengal in aqueous solution using a Ti/TiO_2 mesh electrodes [37]. However, often severe experimental conditions like large excess of catalyst (0.25–2.0 g/L and 5–50 ppm rose Bengal) compared to the contaminant have been applied in degradation experiments combined with high irradiation power [36].

2. Experimental section

2.1. Synthesis of carbon nitride

The bulk tri-*s*-triazine based CNTs were prepared by thermal condensation of melamine in a quartz tube in the flow of argon. The melamine (Merck) was heated firstly to 380 °C with a rate of 5 °C min^{-1}, then to 600 °C by 1.5 °C min^{-1} in a quartz tube, and kept at this temperature for four hours. The obtained yellow powder was denoted as CNT-1. The porous g-C_3N_4 was prepared according to