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Water-assisted ions in situ intercalation for porous polymeric graphitic carbon nitride nanosheets with superior photocatalytic hydrogen evolution performance

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ABSTRACT

Two-dimension layered polymeric carbon nitride possessing unique electronic structure and high specific surface area exhibits immense potentials for visible light driven photocatalytic activity for hydrogen production by the decomposition of water molecules. Herein, porous polymeric carbon nitride nanosheets were obtained by lithium chloride ions in situ intercalating bulk materials in thermal polycondensation process and followed by liquid exfoliation in water. The porous nanosheets show two-dimension layered structure with the thickness of 2–3 nm, a high density in-plane pores with 2–3 nm diameter, a higher surface area (186.3 m^2 g^{-1}), enlarged bandgap (by 0.16 eV), prolonged charge carrier lifetime, enhanced electronic transport ability, increased charge carrier density and improved photocurrent responses, which could significantly give rise to photocatalytic activity. The results highlight the crucial role of 2D porous structure, high specific surface area and unique electronic structure on the photocatalytic performance of polymeric carbon nitride materials.

1. Introduction

The exploration of highly efficient photocatalyst for hydrogen production from water splitting is regarded as a promising strategy for converting sustainable solar energy to hydrogen energy [1]. Photocatalytic efficiency is dominated by photo-generation of charge carriers in semiconductor, which is determined by four major contributors. In sequence, they are efficiencies of (1) light absorption, (2) exciton diffusion, (3) charge formation and separation and finally (4) charge transport and collection [2]. Hence, searching superior photocatalyst to improve photo-induced charge carrier efficiency in the process of photocatalytic reaction is necessary. Carbon nitrides, a great semiconductor has attracted considerable interesting as a promising metal-free visible-light photocatalyst owing to the merits of unique electronic structure, abundance, high stability and chemical tenability [3,4]. The CNs based on heptazine building blocks, known as melon is often called graphitic carbon nitride (g-C_3N_4, noted as CN in this paper) and its structure is similar to graphite [5,6]. The crystal structure of polymeric graphitic carbon nitride is depicted in Fig. 1. The layers are composed of tri-s-triazine motifs and stacked in an ABA-fashion combined by weak van der Waals forces [7]. In the past year, many strategies were conducted to enhance photocatalytic activity of CNs, such as doping heteroatoms [8,9], constituting heterojunction [10–13], sensitizing with organic dyes [14] and controlling morphology [15–19]. For semiconductors, morphology is an important parameter due to its remarkable effect on the electronic spectrum of charge carrier and optical properties of materials [20,21]. Morphology also modifies the strength of the electron-hole Coulomb coupling due to the small dielectric constant of the surrounding media increasing the exciton binding energy in layered materials [22]. In addition, layered materials significantly increase the specific surface area providing abundant reaction sites. In this regards, the delamination of layered CNs into ultrathin nanosheets has proved to an effective method to enhance photocatalytic efficiency both via the exposure of reaction active sites and optimizing of light harvesting, charge separation and percolation. According to a predominance of intra-planar transport together with possible inter-planar transitions [23,24], a possible electron transport model is also depicted in Fig. 1. The singlet Frenkel excitons or polaronic charge carriers in conjugated polymers are most probable mobile species for electron transport in polymeric carbon nitride and their electronic transport is predominantly perpendicular to the layer. Consequently, single or a few layered two-dimension CNs is favorable for photocatalysis.

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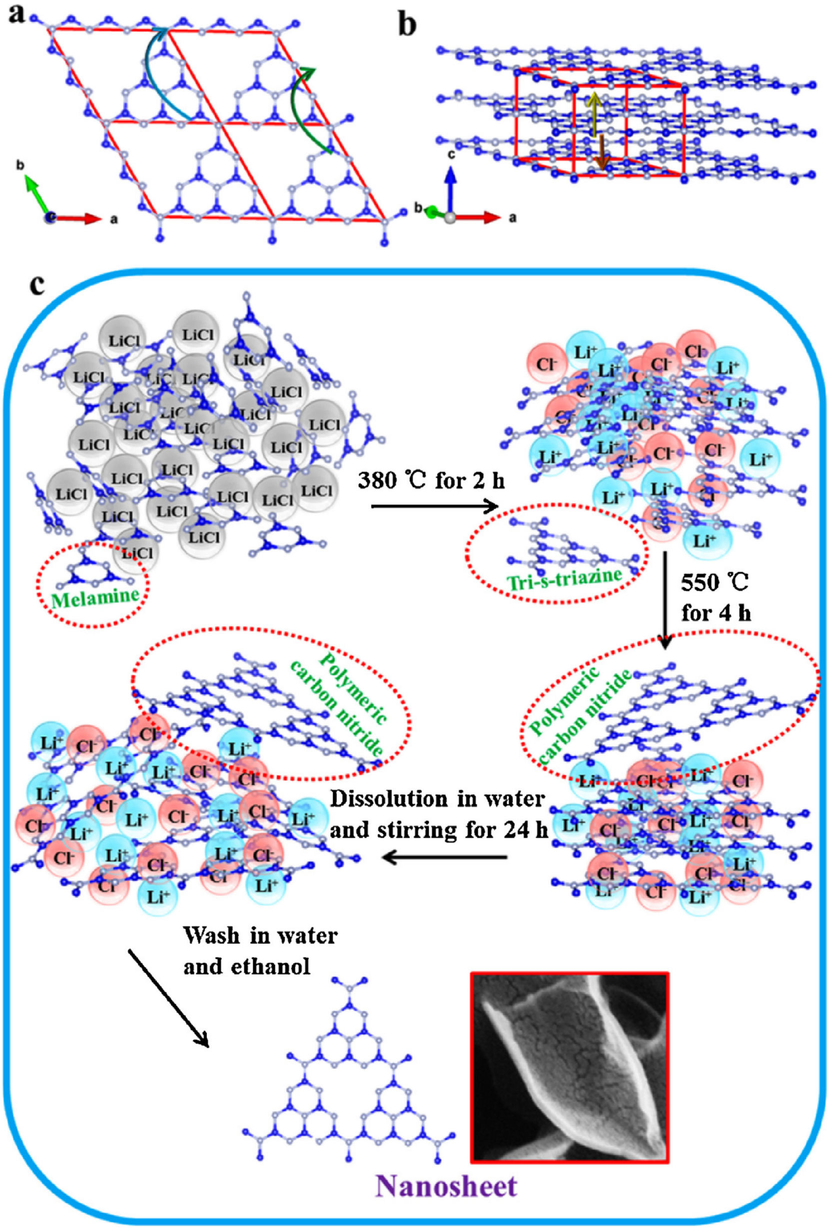

Fig. 1. Idealized CN structure viewed along (a) the c-axis and (b) the slightly tilted b-axis. Probable hopping transport scenarios are depicted: intra-planar (blue and green line), or inter-planar (yellow line) (c) Schematic illustration of the formation of bulk-CN/Li+ Cl- and exfoliation process. The carbon atoms are blue and the nitrogen atoms are gray in atomic model. The units in synthesis process are depicted in red dotted circle. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Immense efforts have been made to achieve 2D layered graphitic polymeric carbon nitrides (g-C_3N_4, remarked as CN) previously. For example, Yang et al. exfoliate bulk g-C_3N_4 using continuous sonication-assisted liquid method [25]. Niu et al. synthesize g-C_3N_4 nanosheet utilizing thermal oxidation [26]. Li et al. prepare porous g-C_3N_4 by chemical oxidation [27]. However, those methods require complex procedure, long-time ultrasonic synthsis (10–16 h), high-temperature oxidation or strong oxidants.

Herein, we reported a two-step method to obtain porous carbon nitride nanosheets. It indicates the synthesis of porous carbon nitride nanosheets from bulk carbon nitrides by “green” liquid exfoliation in water without additives, toxic solvents or pre-intercalation steps in second step. Remarkably, the nanosheets with 2–3 nm in thickness and high density in-plane pores with 2–3 nm diameter exhibit superior photocatalytic efficiency for visible-light-driven hydrogen production from water splitting in comparison with bulk CNs.

2. Results and discussions

2.1. Material characterization

As depicted in Fig. 1c, the basis of this method is that the layered structure motifs (tris-s-triazine) forms via melamine rearrangements at round 380 °C for 2 h [28]. Lithium chloride loses crystal water at 380 °C and lithium chloride ions situate in channels running along the stacking direction. When the temperature increases to 550 °C, polymeric graphitic carbon nitride containing lithium chloride ions in inter-planar channels obtain and is marked as bulk-CN/Li^+ Cl^-. The efficiency of exfoliation will be highest, when the surface energy of solvent matches well with that of CNs [29]. According to zhang et al. calculation, the surface energies of CNs and water are 115 mJ/m^2 and ~102 mJ/m^2 respectively [30]. Therefore, water is a great candidate for exfoliation of bulk carbon nitrides. The bulk-CN/Li^+ Cl^- is suspended in water (1 mg/ mL) under vigorously