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Facile one-step synthesis of hollow mesoporous g-C_3N_4 spheres with ultrathin nanosheets for photoredox water splitting

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ABSTRACT

A facial, one-step soft templating method to synthesize the hollow mesoporous g-C_3N_4 spheres with high surface area and high porosity was developed, which taking advantage of both supramolecular assembly of cyanuric acid and melamine through hydrogen bonds and the structure-directing character of ionic liquid. The influence of solvent and ionic liquid content on the assemble behavior of the cyanuric acid-melamine complex is studied in detail, respectively. It is found that the as-prepared hollow g-C_3N_4 spheres possess plenty of mesopores with a high surface area, which is related to the release of volatile domains and decomposition of ionic liquids. Moreover, as-prepared g-C_3N_4 exhibit improved light absorption in visible ranges, faster separation rate of photogenerated hole-electron pairs than the bulk carbon nitride. Besides, the as-prepared hollow mesoporous carbon nitride exhibits almost 30 times higher than traditional g-C_3N_4 which calcined by melamine for the photocatalytic hydrogen evolution reaction under visible light irradiation, which may be caused by the fact that the high surface area is beneficial for improving light absorption in visible ranges, and finally enhancing the H_2 evolution rate. This method paves new opportunities for designing other catalysts with high surface area.

1. Introduction

Solar energy harvest and conversion into a usable energy form by photocatalysts has been regarded to be a potential and promising approach to settle the increasing energy crisis and environmental pollution [1–3]. Water splitting into hydrogen using semiconductors, as one of the ideal strategy for converting solar energy into clean energy, plays an essential role in this system since the founding of TiO_2 electrode by Fujishima and Honda [4–6]. Among numerous photocatalysts, graphitic carbon nitride (g-C_3N_4) achieves considerable attention due to the unique optical, chemical, and catalytic activities [7–11]. Additionally, g-C_3N_4 can be synthesized by one step thermally condensing precursors, such as urea, thiourea, cyanamide and melamine, which endows it the enormous application prospect, such as hydrogen generation, oxygen evolution, CO_2 reduction and pollutant elimination [12–15].

Nevertheless, the intrinsic drawbacks of bulk g-C_3N_4, including the low surface area, the high recombination efficiency of photogenerated electron-hole pairs and poor mass transfer, limit the further enhancement of photocatalytic activities [16,17]. The main works for improving the charge carrier separation center on the doping with nonmetal elements and heterostructure construction [18–20]. The textural modification is another successful and efficient way to improve electronic and optical properties [6,21]. Hollow structured materials with high surface area have been certified the high activities in the catalysis and can also be applied in drug delivery, nanodevices, gas storage and batteries [22,23].

Up to date, most of studies utilized the hard-templating method to fabricate the 3D structured porous g-C_3N_4 with high surface area and the common templates are silica spheres, mesoporous silica or SBA-15 [22,24–26]. However, the hazardous reagents including HF, NaOH solution and NH_4HF_2 are usually used to remove the templates, which has a bad influence to the environment [27,28]. While, soft templating method is a facile, one-step way to fabricate the g-C_3N_4 with high surface area [29–31]. Ionic liquid, as a novel green solvent, has been used as templates or co-templates to synthesize the porous materials [32–34]. In our previous work, the

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core-shell structured mesoporous silica spheres were synthesized by using CTAB and protic ionic liquid as the templates [35]. It is found that ionic liquid can self-assemble into micelles which induce the porous materials. Such strategy can be applied in the construction of hollow mesoporous g-C_3N_4 spheres. The interaction between the template and precursors plays an important role to the final texture and morphology of carbon nitride. Thus, finding a suit carbon nitride precursor is also vital for this system. Nowadays, the cyanuric acid-melamine complex formed by hydrogen bonds between cyanuric acid and melamine can lead to 3D g-C_3N_4 with a tunable morphology based on the solvent used in this process. Peer and co-workers [28] synthesized the mesoporous carbon nitride using cyanuric acid-melamine complex as the precursor in the water. Guo et al. [7] obtained the phosphorus-doped hexagonal tubular carbon nitride with the layered stacking structure by using supramolecular precursor cyanuric acid-melamine complex. While, the surface area of the obtained g-C_3N_4 was as lower as about 40 m [2]/g. It is urgent to design the novel strategy to obtain the hierarchical porous structured carbon nitride with high surface area.

Herein, we develop a facial, one-step soft templating method to synthesize the hollow mesoporous g-C_3N_4 spheres with high surface area and high porosity, utilizing both cyanuric acid-melamine complex formed by hydrogen bonds and ionic liquid. The influence of solvent and ionic liquid content on the assemble behavior of the cyanuric acid-melamine complex is studied in detail, respectively. The photocatalytic activity of as-fabricated hollow mesoporous structured g-C_3N_4 is tested by the photocatalytic hydrogen evolution reaction under visible light irradiation. Besides, the relationship between structure and photocatalytic activity is discussed based on the various characterization results and theoretical analysis.

2. Experimental section

2.1. Chemicals

All the chemicals were used without further purification. The ionic liquid (1-butyl-3-vinylimidazolium bromide), melamine and cyanuric acid was purchased from Sinopharm Chemical Reagent Co. Ltd.

2.2. Synthesis of hollow mesoporous g-C_3N_4 spheres

Typically, 0.5 g of melamine and 0.5 g of cyanuric acid were dispersed in 15 mL and 20 mL Dimethyl sulfoxide (DMSO), respectively. Then, a certain amount of ionic liquid (0.02–0.1 g) were added into the cyanuric acid solution and keep stirring for 1 h. The melamine solution was dropwise into the cyanuric acid solution. After stirring for another 2 h, the mixture was centrifuged and denoted as CN-C. CN-C were redispersed with 50 mL of ethanol or acetone and stirred for another 20 h. The final powder was centrifuged and dried at 50 °C in the oven, then calcined at 550 °C for 4 h in the nitrogen, which was named as CN-E or CN-A. g-C_3N_4 calcinated from melamine was marked as CN.

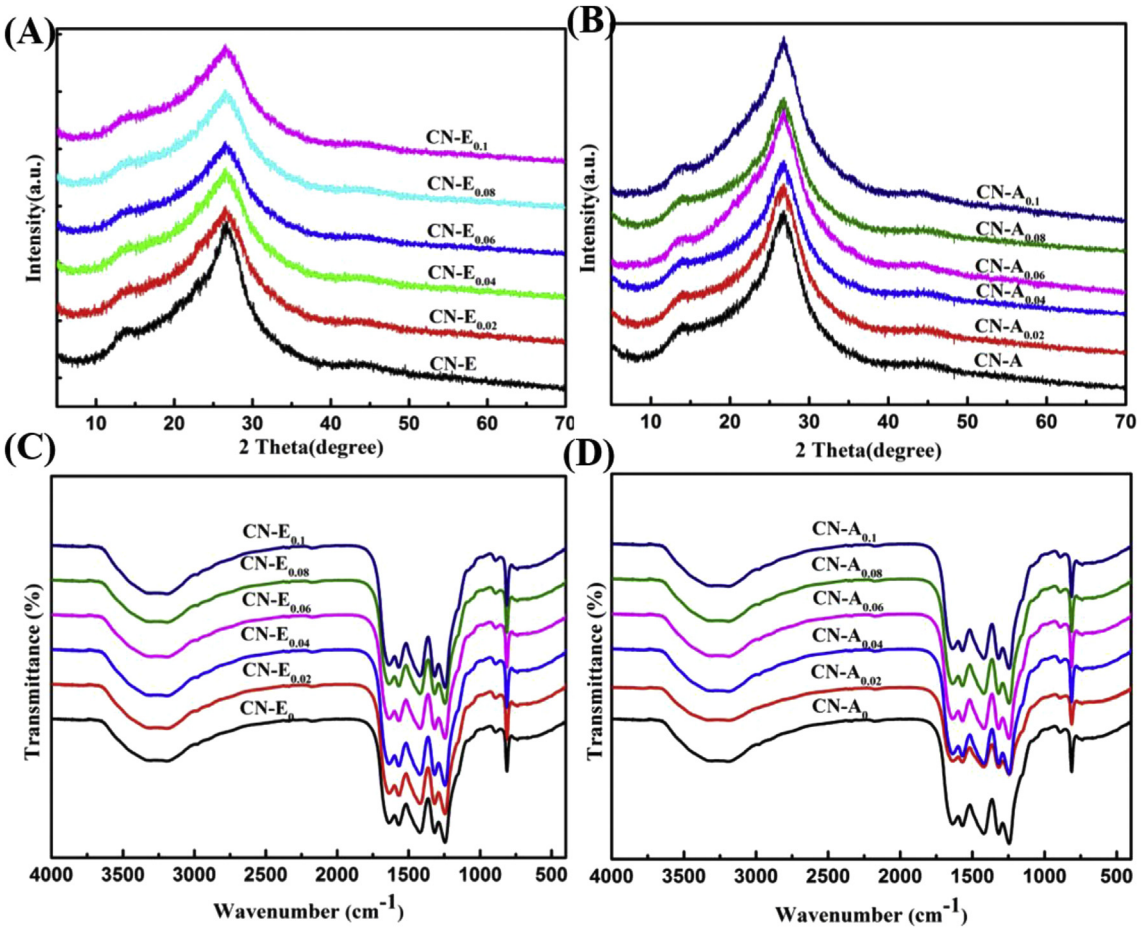

Fig. 1. XRD patterns (A, B), FTIR figures (C, D) of as-prepared hollow mesoporous carbon nitride spheres. (A colour version of this figure can be viewed online.)