



Research Paper

Oxygen-doped nanoporous carbon nitride *via* water-based homogeneous supramolecular assembly for photocatalytic hydrogen evolutionJing-Wen Zhang^{a,b}, Si Gong^{a,b}, Nasir Mahmood^{a,b}, Lun Pan^{a,b}, Xiangwen Zhang^{a,b}, Ji-Jun Zou^{a,b,*}^a Key Laboratory for Green Chemical Technology of the Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin, 300072, China^b Collaborative Innovative Center of Chemical Science and Engineering (Tianjin), Tianjin, 300072, China

ARTICLE INFO

Keywords:

Carbon nitride
Photocatalysis
Supramolecular assembly
Oxygen-doping
Hydrogen evolution

ABSTRACT

Graphitic carbon nitride (g-C₃N₄) has emerged as a promising photocatalyst, but poor charge separation and low surface area limit its activity. Here, we report a hydrothermal method to generate hydrogen bonded supramolecular complex *via* water-based homogeneous supramolecular assembly, which is a promising precursor to fabricate porous and oxygen-doped g-C₃N₄. The hydrothermal treatment provides a homogeneous environment for hydrolysis of melamine to produce cyanuric acid and reaction of cyanuric acid with remained melamine to create the in-plane ordering and hydrogen bonded supramolecular complex. The complex can template uniform nanoporous structure and also provide an opportunity for O-doping in the g-C₃N₄ network upon calcination in air. The resulted g-C₃N₄(GCN-4) possesses high surface area, well-defined 3D morphology and oxygen-dopant in the lattice. Subsequently, the visible light absorption, charge separation, and wettability are considerably enhanced. This catalyst exhibits higher hydrogen evolution rate by 11.3 times than the bulk g-C₃N₄ under visible light irradiation, with apparent quantum efficiency of 10.3% at 420 nm.

1. Introduction

Graphitic carbon nitride (g-C₃N₄) has attracted widespread attention in photocatalytic hydrogen evolution and environmental remediation as a promising metal-free and visible-light-responsive photocatalyst [1–3]. However, high recombination rate of charge carriers, low surface area and low electrical conductivity limit the activity of g-C₃N₄ synthesized by traditional methods, which can be improved by controlling the morphology, electronic and optical properties through nanostructuring, heteroatom doping and copolymerization [4–6]. In particular, simultaneous utilization of nanostructure design, high porosity and heteroatom doping such as oxygen can increase the active surface area and optimize the electronic structure to broaden light-absorption and effective charge separation. Porous g-C₃N₄ can be fabricated by soft templating method where organic directing agents lead the pore formation but need to be eliminated at the end. As well, hard templating uses ordered 2D or 3D porous solid materials and requires harsh conditions to remove the template to achieve final product [7–19]. In contrast to conventional templating strategies, supramolecular preorganization approach provides an easy control over structure by assembling monomers into supramolecular aggregates *via* hydrogen bonding. Through calcination, the removal of hydrogen bonds results in

higher degree of freedom and yields well-organized 3D porous network, while it does not require any external template [1,20]. Along with the good control over morphology, the supramolecular complex strategy also provides an opportunity to tune the electronic structure through the doping of suitable heteroatoms.

Thus, extensive research has been carried out on the development of nanostructured g-C₃N₄ materials through supramolecular preorganization by linking melamine with triazine derivatives like cyanuric acid and trithiocyanuric acid to produce hydrogen-bonded molecular assemblies [20–24]. The solvent plays a crucial role in the preorganization process, because it can influence the equilibrium geometry and dynamic behavior of the monomers [23,25,26]. However, melamine and cyanuric acid are just slightly dissolvable in most solvents at room temperature, thus it is impossible to provide a homogeneous chemical reaction environment. Till now, dimethylsulphoxide and chloroform have been explored as the solvent to produce ordered hydrogen-bonded supramolecular structures because of their capability to dissolve melamine and cyanuric acid, but their use is not environmentally friendly [25,27]. On the other hand, nonmetal heteroatom doping can modify the local electronic structure which can enhance the visible light harvesting capability, charge separation efficiency and thus photocatalytic activity. Specially, oxygen can play more effective role in this regard

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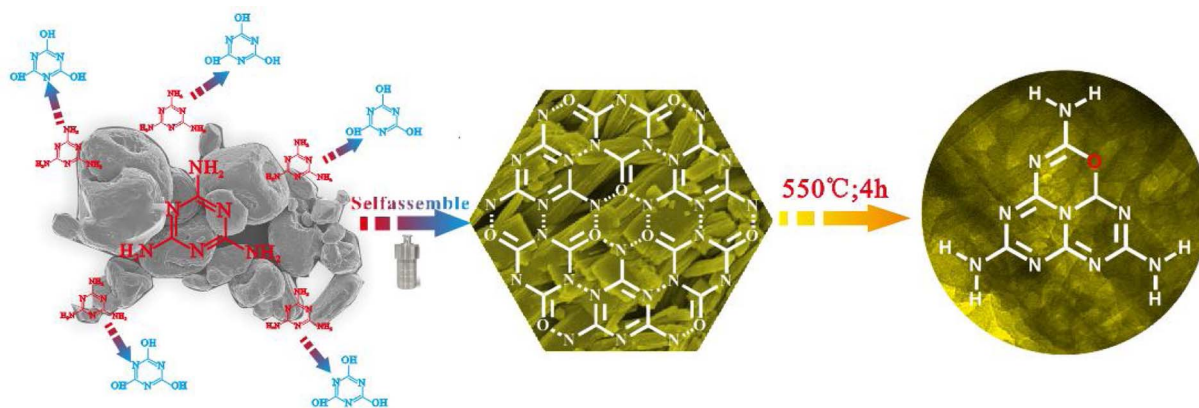
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<http://dx.doi.org/10.1016/j.apcatb.2017.09.003>

Received 18 May 2017; Received in revised form 28 July 2017; Accepted 2 September 2017

Available online 05 September 2017

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Scheme 1. Illustration of fabrication of O-doped porous g-C₃N₄ from hydrogen bond-induced supramolecular precursor assembled under hydrothermal treatment.

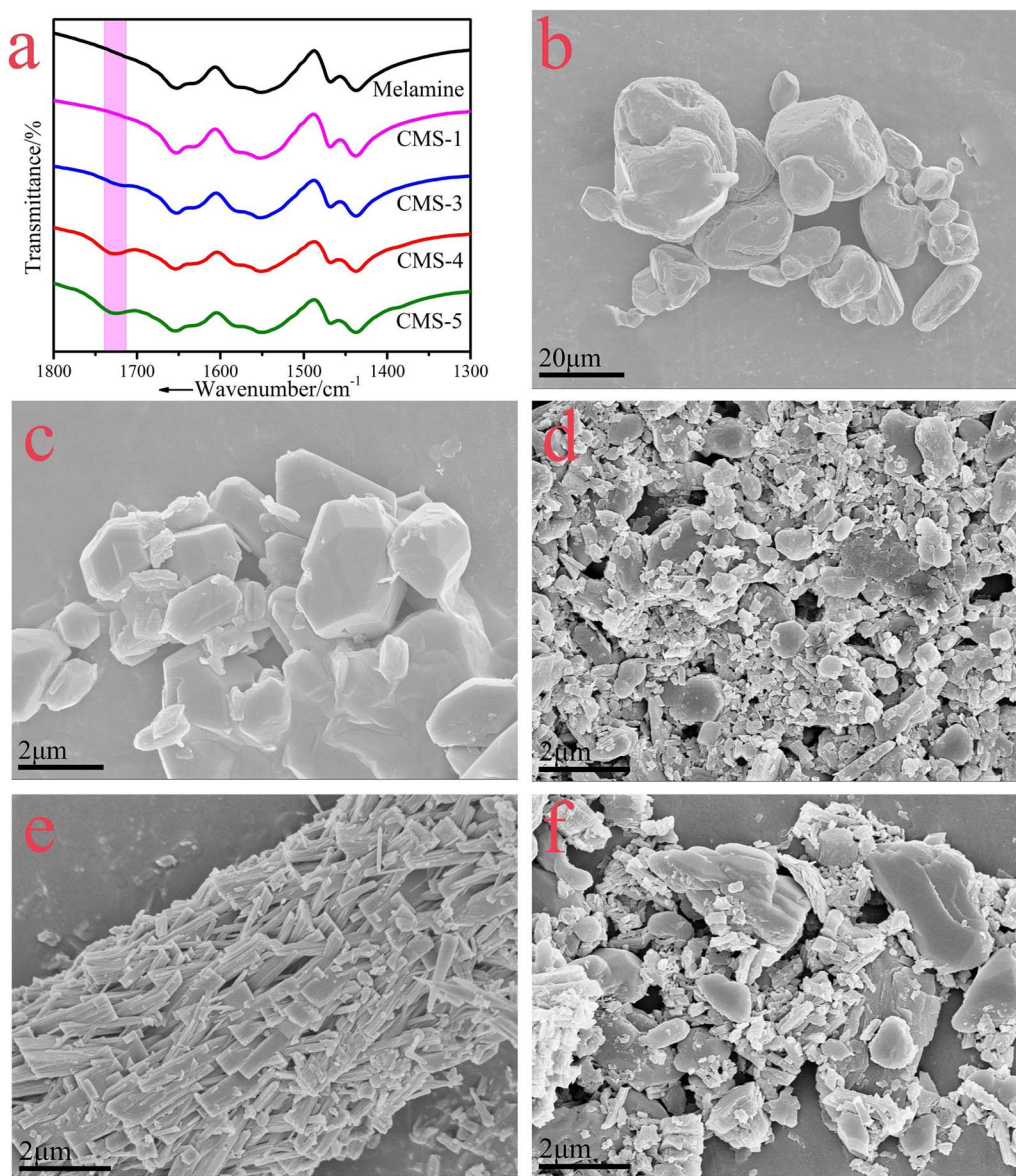


Fig. 1. a) FTIR spectra of pristine-melamine and CMS. The SEM images of (b) pristine melamine, (c) CMS-1, (d) CMS-3, (e) CMS-4 and (f) CMS-5.

[28–35]. Oxygen-doped g-C₃N₄ have been synthesized by treating g-C₃N₄ with H₂O₂ or under oxygenated atmosphere, and treating melamine with H₂O₂ to be the precursor [28–34]. But these strategies do not provide easy control on structure, especially for the later one, because

such treatment is a heterogeneous solid-liquid reaction, which limit the formation of hydrogen bonds on the surface of melamine that may induce inhomogeneity and limited bonding [29]. So we aim to search an environmentally benign and cheap solvent that can dissolve melamine,

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