



Constructing bio-templated 3D porous microtubular C-doped g-C₃N₄ with tunable band structure and enhanced charge carrier separation

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ABSTRACT

For the first time, the bio-templated porous microtubular C-doped (BTPMC) g-C₃N₄ with tunable band structure was successfully prepared by simple thermal condensation approach using urea as precursors and kapok fibre which provides a dual function as a bio-templates and in-situ carbon dopant. Prior to the thermal condensation process, the impregnation strategies (i.e. direct wet and hydrothermal impregnation) of urea on the treated kapok fibre (t-KF) were compared to obtained well-constructed bio-templated porous microtubular C-doped g-C₃N₄. The details on a physicochemical characteristic of the fabricated samples were comprehensively analyze using X-ray diffraction (XRD), Fourier transform infrared (FTIR), X-ray photoelectron spectroscopy (XPS), Field-emission scanning electron microscopy (FESEM), Transmission electron microscopy (TEM), N₂ adsorption-desorption, Thermogravimetric (TGA), and UV–vis spectroscopy. Our finding indicated that the hydrothermal impregnation strategy resulted in well-constructed microtubular structure and more carbon substitution in sp²-hybridized nitrogen atoms of g-C₃N₄ as compared to the direct wet impregnation. Also, compared to pure g-C₃N₄, the fabricated BTPMC g-C₃N₄ exhibited extended photoresponse from the ultraviolet (UV) to visible and near-infrared regions and narrower bandgap. The bandgap easily tuned with the increased t-KF loading in urea precursor which responsible for in-situ carbon doping. Moreover, as compared to pristine g-C₃N₄, dramatic suppression of charge recombination of the BTPMC g-C₃N₄ was confirmed through photoluminescence, photocurrent response, and electrochemical impedance spectroscopy. The resultants BTPMC g-C₃N₄ possesses more stable structure, promoted charge separation, and suitable energy levels of conduction and valence bands for photocatalysis application.

1. Introduction

Photocatalysis is widely used for hydrogen production, CO₂ photo-reduction well as organic contaminants decomposition. The ideal photocatalytic material should possess a moderate band gap, which absorbs light in the visible range and is efficient in separating, collecting and transporting charges for the chemical processes. Recently, graphitic carbon nitride (g-C₃N₄) has emerged as an innovative

photocatalyst with tunable band gaps of 1.8–2.7 eV that allow the harvesting of visible light ranging from 460 to 698 nm (potentially utilise 13–49% of solar energy, though the photocatalytic activity may reduce at a longer wavelength). The g-C₃N₄ possesses a stacked 2D structure, which could regard as a nitrogen heteroatom-substituted graphite framework consisting of p-conjugated graphitic planes formed via sp² hybridisation of carbon and nitrogen atoms. This material is made from earth-abundant, inexpensive C and N containing precursors

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(e.g., urea, melamine), is biocompatible with no reported toxicity, is resistant to photo-corrosion, and remains chemically stable in harsh environments.

However, pure g-C₃N₄ suffers from the insufficient sunlight absorption, low surface area and the fast recombination of photo-induced electron-hole pairs, resulting in low photocatalytic activity. To substantially utilise the solar energy, it is far from satisfactory to make photocatalysts only respond to UV (~ 5%) and visible light (~ 43%), with the near-infrared (NIR) photons waste, which makes up a significant portion ~ 52% of the whole solar spectrum. To date, only a few studies report on NIR photocatalysis [1].

Element doping is known to be an efficient method to tune the unique electronic structure and the band gap of g-C₃N₄, which considerably broaden the light responsive range and enhance the charge separation [2]. Up until today, there are several elements has been used as dopants in g-C₃N₄ which differentiated into metal (K, Na, Fe, Cu, Ce, Co, Eu, Mo, W, Y, Zr) and non-metal (P, S, O, C, N, B, F, I, Br) dopants [2]. In comparison with a metal dopant, the non-metal dopant is relatively low-cost and enhanced the mobility of photo-induced charge carriers. In contra, the metal dopants or nanoparticles are more expensive (e.g., noble metal loading), and they may leach or deactivated in complex aquatic chemistries (e.g., metals fouled by natural organic matter, NOM, or sulfide) [3]. In the present study, the selection of C as dopants elements was due to its earth-abundant, low-cost, non-toxic dopants as compared to other non-metal dopants. Furthermore, the utilising C as the dopant material in g-C₃N₄ are due to its comparable atomic size with nitrogen, small ionisation energy, eco-friendly, higher stability and simple synthesis methods [4]. Besides, the density functional theory (DFT) simulations indicated that C-doped g-C₃N₄ showed a thermodynamically stable structure, promoted charge separation, and suitable energy levels of conduction and valence bands for photocatalytic oxidation, compared to phosphorous-doped g-C₃N₄ [3].

The previous study utilised barbituric acid was used as a source of carbon or doping because it can be incorporated into the supramolecular complex of melamine and cyanuric acid via hydrogen bonding or electrostatic interactions to promote efficient doping [3,5]. Later, the porous carbon-doped g-C₃N₄ nanosheets photocatalysts (NSs-APAM) were synthesised using anionic polyacrylamide (APAM) as the intercalator and carbon source via the thermal treatment method. In the same year of 2017, the post granulation thermal oxidation treatment resulted in in-situ doping of carbon leading to improved photophysical properties compared to pristine g-C₃N₄. Also, the self-carbon doping also has been reported by the previous study using melamine as precursor [6,7].

Recently, increasing number of researchers from China's researcher were emphasising the utilisation of kapok fibre as bio-templates in metal oxides preparation for various application. For instance, the three-dimensional (3D) carbonised kapok fibre/nickel oxide, manganese oxide and cobalt-nickel binary oxide hybrids for high-performance electrode materials of supercapacitors [8–11]. Moreover, the kapok fibre also has been used in the preparation of the 3D hierarchic heterojunction photocatalysts assembled from interlinked MoS₂/CoAl-LDH (CoAl-layered double hydroxide)@carbon micron fibre for visible-light degradation of Congo Red [12]. On the other hand, the SnO₂ hollow fibre for application in dye-sensitised solar cells also has successfully prepared by researchers from South Korea using kapok as a bio-templates [13]. However, to the best of our knowledge, it is tough to find the utilisation of bio-templated in synthesis carbon doped g-C₃N₄ in the open literature. Most of the time, C-doped photocatalyst prepared via the bio-templated synthesis was only focusing on the metal oxides such as TiO₂, MnO, and ZnO [14–19]. On top of that, the utilisation of kapok fibre as bio-templates and in-situ carbon dopant in the preparation of carbon doped g-C₃N₄ is still not yet reported.

Here, for the first time, we reported the facile synthesis of g-C₃N₄ using urea as a precursor and kapok fibre as bio-templates and in-situ carbon dopant sources. Kapok fibre as cellulose-based materials is used

as bio-templates due to its insolubility, which renders them more appropriate for bio-replication than for nanoparticle growth control. The incorporated urea precursor could be bound to the kapok fibre via electrostatic interaction and hydrogen interaction because the electron-rich oxygen atoms of the polar hydroxyl groups of cellulose are expected to interact with the urea in aqueous solution. Our finding indicates that the resultants bio-templated microtubular carbon doped g-C₃N₄ show excellent enhancement in charge carrier separation for high-performance photocatalytic material.

2. Experimental

2.1. Materials

Kapok fibre as bio-template were obtained from Perusahaan Bonda, Kuala Kangsar, Perak, Malaysia. Urea and isopropanol (IPA), was provided by QReC Malaysia. Sodium Chlorite (NaClO₂), Sodium Sulphate (Na₂SO₄) (80%), Bisphenol A (BPA), Ammonium Oxalate (AO), and 1,4-benzoquinone (BQ) were procured from Sigma Aldrich. All reagents and chemicals were analytical reagent grade, and no purification step was performed.

2.2. Kapok fibre pre-treatment

Before bio-templated synthesis of g-C₃N₄, the kapok fibres (KF) was undergone NaClO₂ pre-treatment to remove the waxy coating and improved hydrophilicity on its surface according to our previous study [20]. About 1 g of KF was added to 1 wt % of the NaClO₂ solution under magnetic stirring for 10 min. Then, the KF suspension was refluxed at 120 °C for 4 h. Finally, the resultant treated KF was washed with running tap water followed by distilled water and dried overnight in an oven at 65 °C. The NaClO₂ pre-treated KF was named as t-KF.

2.3. Synthesis of bio-templated C-doped porous microtubular g-C₃N₄

The bio-templated C-doped porous microtubular (BTCPM) g-C₃N₄ was prepared using facile direct wet and hydrothermal impregnation followed by thermal condensation. Firstly, 50 g of urea in powder form was dissolved in 75 mL of distilled water. Then, a specific amount of t-KF was added to aqueous urea solution under vigorous stirring for 30 min and followed by sonication for 30 min. For direct wet impregnation, the highly-dispersed t-KF in aqueous urea solution was stored in an oven at 60 °C overnight to evaporate the water, then cooling at room temperature to allow urea recrystallisation. On the other hand, for hydrothermal impregnation, the highly-dispersed t-KF in aqueous urea solution was transfer into 150 mL Teflon-lined stainless-steel autoclave, and the autoclave was sealed and heated at 150 °C for 2 h. Finally, the samples from both impregnation strategy were subjected to the thermal condensation process at 500 °C with the heating rate of 5 °C min⁻¹ for 2 h, using porcelain crucible and lids. The same procedures were repeated by varying the loading of t-KF (wt %) ranging from 0.4 to 2.0 wt %. The resultants samples were denoted as D-0.4, D-0.8, D-1.2, D-1.6, and D-2.0 and h-0.4, h-0.8, h-1.2, h-1.6 and h-2.0 for direct wet impregnation and hydrothermal impregnation, respectively.

2.4. Characterisation

The crystallinity of samples was determined by using Siemens X-ray Diffractometer D5000 with CuKα radiation of wavelength 0.15406 nm at 40 kV and 40 mA. The diffracted intensity was measured by scanning range of 2θ = 5–60° with a step speed of 2°/min. Fourier transform infrared (FTIR) spectra of the samples were obtained using Perkin Elmer infrared spectrometer. Fourier Kratos Analytical Axis Ultra DLD photoelectron spectrometer was used to get the X-ray photoelectron spectroscopy (XPS) spectra of the prepared samples, using Al Kα radiation monochromatic source. The morphological study was carried

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