



Fabrication of the protonated graphitic carbon nitride nanosheets as enhanced electrochemical sensing platforms for hydrogen peroxide and paracetamol detection



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ABSTRACT

In this research, graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) is synthesized through the direct pyrolysis of the melamine, and the pristine $g\text{-C}_3\text{N}_4$ is further treated by sufficient protonation and ultrasonication. The resultant $g\text{-C}_3\text{N}_4$ nanosheets, with two-dimensional thin nature, exhibit enhanced ionic conductivity and large specific surface area. Density function theory (DFT) calculations of the electrical properties of the protonated $g\text{-C}_3\text{N}_4$ nanosheets demonstrate that the higher level of protonation enables $g\text{-C}_3\text{N}_4$ to have better conductivity. In addition, the protonated $g\text{-C}_3\text{N}_4$ nanosheets also show excellent electro-catalytic activity and have been employed as electrochemical sensing platforms for the non-enzymatic electrochemical sensing hydrogen peroxide (H_2O_2) and the selective determination of paracetamol (PCM). The results demonstrate that the protonated $g\text{-C}_3\text{N}_4$ nanosheets, as sensor materials, achieve superior electrochemical sensing performance. The exfoliated $g\text{-C}_3\text{N}_4$ nanosheets have great potential for application in further sensor development and biomedical analysis.

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1. Introduction

Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) as a new two-dimensional material has aroused a great deal of interest in recent decades. Owing to its unique physical and chemical properties, $g\text{-C}_3\text{N}_4$ has been applied in catalysis, electronics, biomedical imaging and in sensor fields [1–6]. For sensor applications, $g\text{-C}_3\text{N}_4$ and its composites have been employed to fabricate fluorescent, photo-electrochemical, electrogenerated chemiluminescent (ECL), optical and electrochemical sensors [6–15]. The electrochemical sensing performance of pristine $g\text{-C}_3\text{N}_4$ is limited to its chemical inertness, specific surface area and the conductivity. There have been scarce reports about the fabrication of electrochemical sensors based on $g\text{-C}_3\text{N}_4$. In order to broaden the application of $g\text{-C}_3\text{N}_4$ in electrochemical sensing, various methods have been developed to modify $g\text{-C}_3\text{N}_4$ and enable $g\text{-C}_3\text{N}_4$ to be incorporated

with other nanomaterials when applied in the fabrication of electrochemical sensors [13]. Functionalized $g\text{-C}_3\text{N}_4$ and its composites as electrochemical sensing platforms had been used for H_2O_2 , nitrobenzene, and NADH, glucose and mercuric ions detection [12–15]. Hence, developing a way of tailoring and functionalizing $g\text{-C}_3\text{N}_4$ is a major research task.

There has been some progress in the modifying $g\text{-C}_3\text{N}_4$ that liquid-exfoliation method, chemical oxidation and protonation can be employed to alter the properties of $g\text{-C}_3\text{N}_4$ [16–20]. Liquid-phase exfoliation methods were carried out through intercalation and surface passivation with solvent molecules to exfoliate $g\text{-C}_3\text{N}_4$ [16–18]. This method was then followed by sonication treatment or thermal shock. Though this method can achieve exfoliation of $g\text{-C}_3\text{N}_4$, suitable solvents are required for the preparation of uniform dispersion and the sonication time is too long. The chemical oxidation can be regarded as an efficient way for exfoliating $g\text{-C}_3\text{N}_4$ and introducing some active groups to $g\text{-C}_3\text{N}_4$. The pristine $g\text{-C}_3\text{N}_4$ when treated with oxidizing agent will produce hydroxyl and carboxyl groups on its basal plane, thus improving the chemical activity of $g\text{-C}_3\text{N}_4$ [19]. The key to the chemical oxidation of $g\text{-C}_3\text{N}_4$ is the selection of proper reactants and oxidants, which exerts a

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great effect on the degree of oxidation and the planar atomic structure of $g\text{-C}_3\text{N}_4$ [19,21]. Owing to the rich nitrogen in carbon nitride, direct protonation is a very convenient modification route. The protonation of $g\text{-C}_3\text{N}_4$ was firstly proposed by Zhang et al. The protonation has been commonly recognized as an efficient way to improve the specific surface area and ionic conductivity of $g\text{-C}_3\text{N}_4$ [20,22].

Hydrogen peroxide (H_2O_2) is often used as a versatile oxidant in various fields such as food, pharmaceutical industry and environmental analysis. H_2O_2 is also considered as a signaling molecule in various biological processes such as vascular remodeling, immune cell activation and root growth [23–25]. In addition, H_2O_2 is a side product generated from some biochemical reactions that some enzymes, such as glucose oxidase (GOx) and alcohol oxidase (AOx), are taken as catalysts. Due to the significance of H_2O_2 in the academic research of biological systems and practical applications, it is imperative to develop efficient methods for H_2O_2 detection. The non-enzymatic H_2O_2 sensor can achieve accurate H_2O_2 detection with high sensitivity. Pharmaceutical analysis plays an important role in drug dosage control and quality monitoring. Paracetamol (N-acetyl-p-aminophenol, acetaminophen, PCM) is the most widely used antipyretic and analgesic drug in the world. PCM is commonly applied to reduce fever and relieve colds and pain. However, the clinical experiments had verified that overdoses of PCM would cause acute liver necrosis, inducing morbidity and mortality in humans because of the toxic metabolite accumulation [26–28]. Hence, developing simple and accurate approaches to detecting PCM is very significant in the pharmaceutical management. The electrochemical method is preferred to be used in the PCM detection, because it is very fast, simple and low-cost and can also achieve good accuracy.

In this paper, a simple method was proposed for the protonation and exfoliation of the pristine $g\text{-C}_3\text{N}_4$, and the as-prepared $g\text{-C}_3\text{N}_4$ nanosheets exhibited thin layers and two-dimensional structure. Various techniques were used to characterize the protonated $g\text{-C}_3\text{N}_4$ nanosheets. Simulation and density function theory (DFT) calculations were used to study the structures and electrical property of the protonated $g\text{-C}_3\text{N}_4$ nanosheets, and the results demonstrated that the high level protonation enabled $g\text{-C}_3\text{N}_4$ to have good conductivity. Furthermore, the protonated $g\text{-C}_3\text{N}_4$ nanosheets modified electrode was successfully utilized to achieve the electro-catalytic oxidation of H_2O_2 and highly selective determination of PCM with a wide linear range and low detection limit. The protonated $g\text{-C}_3\text{N}_4$ nanosheets modified electrode presented good anti-interference performance and excellent stability.

2. Experimental

2.1. Chemicals and apparatus

Analytical grade melamine (Shanghai Chemical Reagents Company, China) was recrystallized before use. The phosphate buffer solutions (PBS) were prepared from NaH_2PO_4 and Na_2HPO_4 . Paracetamol (PCM), dopamine (DA), ascorbic acid (AA), 4-aminophenol, caffeine and chitosan (CTS, M.W. 100,000–300,000, deacetylation degree $\geq 95\%$) were purchased from Sigma-Aldrich Chemical Reagent Company (Shanghai, China). All reagents were analytical grade. Dipyrrone, aspirin, naproxen, penicillins and other drugs were purchased from a local pharmacy. All the other reagents were analytical reagent grade, and used without further purification. All water used for experimentation in this work was re-distilled.

Transmission electron microscope (TEM: Tecnai-12, the accelerating voltage: 120 kV) and high resolution transmission electron

microscopy (HRTEM: Tecnai-G2 F30 S-Twin, the accelerating voltage: 300 kV) were utilized to characterize the morphologies of the $g\text{-C}_3\text{N}_4$ samples. The energy-dispersive X-ray (EDX) analysis was also conducted on the Tecnai-G2 F30 at the accelerating voltage of 300 kV. X-ray diffraction (XRD) patterns of the powders were collected with a 2θ range from 5° to 50° on a Bruker AXS D8 ADVANCE X-ray diffractometer with $\text{Cu}/\text{K}\alpha$ radiation (1.5406\AA). X-ray photoelectron spectroscopy (XPS) technology was used to study the bonding states of the elements on an EASY ESCA spectrometer (VG ESCA LAB MKII). The Fourier transform infrared spectroscopy (FTIR) measurements were carried out on a Varian Cary 610/670 FTIR microspectrometer, with the prepared powders diluted in KBr pellets. The Brunauer-Emmett-Teller (BET) surface area (SBET) was obtained by nitrogen adsorption/desorption isotherm measurements at 77 K on a Micromeritics Accelerated Surface Area and Porosimetry (ASAP) 2020 system, and the corresponding pore diameter distributions were calculated using the BJH (Barrett–Joyner–Halenda) method. Electrochemical experiments were performed with a CHI 660A electrochemical workstation (Chenhua Instruments Company, Shanghai, China) with a conventional three-electrode system. The acid density of the protonated $g\text{-C}_3\text{N}_4$ was determined using the non aqueous acid–base titration method.

2.2. Synthesis and protonation of $g\text{-C}_3\text{N}_4$

The $g\text{-C}_3\text{N}_4$ powders were synthesized via direct pyrolysis of the melamine method based on the report [29], but some modification was made for this reported method. Melamine was set in a porcelain combustion boat with a cover and put into a tube furnace. In the first step, it was heated to 500°C and held at this temperature for 2 hours. It was then heated again to 550°C and held at this temperature for 6 hours. The above heating procedures must be in the nitrogen atmosphere. When cooled to room temperature, the porcelain boat was taken out and the pale yellow powdered $g\text{-C}_3\text{N}_4$ was prepared. The typical protonation was carried out by stirring $g\text{-C}_3\text{N}_4$ with hydrochloric acid (HCl, 37%) for 3 hours at room temperature, centrifugal washing with water until the neutral condition and drying at 105°C in air-circulating oven overnight, which was based on the literature [20]. The as-prepared sample was denoted as the $g\text{-C}_3\text{N}_4 \text{H}^+$. The $g\text{-C}_3\text{N}_4 \text{H}^+$ was further exfoliated $g\text{-C}_3\text{N}_4$ using concentrated nitric acid (HNO_3 , 60%) and ultrasonication. The as-obtained $g\text{-C}_3\text{N}_4 \text{H}^+$ powder were put into the concentrated HNO_3 and stir the mixture for 1 hour. The dispersion was then heated to 80°C and ultrasonically treated for 4 hours. Finally, the mixture was centrifugally washed with water until it reached a neutral condition and dried at 60°C in a vacuum drying oven. Finally, the as-prepared product was the protonated $g\text{-C}_3\text{N}_4$ nanosheets.

2.3. Fabrication modified electrode

Firstly, the glassy carbon electrodes (GCEs) were firstly polished with α -alumina powders, then rinsed with deionized water after each polishing step. Secondly, these electrodes were successively sonicated in 1:1 nitric acid, acetone and deionized water. Finally, the GCE was dried at room temperature.

The protonated $g\text{-C}_3\text{N}_4$ nanosheets, the $g\text{-C}_3\text{N}_4 \text{H}^+$ and the pristine $g\text{-C}_3\text{N}_4$, as modifier materials, were attached onto the GCE surfaces using the biopolymer chitosan (CTS) as an immobilization matrix. The modifier materials including the pristine $g\text{-C}_3\text{N}_4$, $g\text{-C}_3\text{N}_4 \text{H}^+$ and the protonated $g\text{-C}_3\text{N}_4$ nanosheets were added into CTS solutions to prepare suspensions, respectively. $10 \mu\text{L}$ of this suspension was dropped onto the GCE surface and allowed to dry at room temperature.

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