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## Energy-level dependent H<sub>2</sub>O<sub>2</sub> production on metal-free, carbon-content tunable carbon nitride photocatalysts

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### ABSTRACT

Light-driven production of H<sub>2</sub>O<sub>2</sub> from water and molecular oxygen could be a promising way for obtaining both solar fuels and fundamental chemicals. During that process, the H<sub>2</sub>O<sub>2</sub> yield is strongly dependent on the reaction pathway associated with two-electron reduction of dioxygen by the photo-generated electrons. Herein, we synthesized a series of metal-free, carbon-content tunable carbon nitride photocatalysts (named C<sub>3</sub>N<sub>4</sub>-Carbon) by a facile hydrothermal reaction and subsequent thermal treatment at appropriate temperatures. The energy levels of the C<sub>3</sub>N<sub>4</sub>-Carbon catalysts vary with the carbon doping level, which is conveniently tuned by changing the initial glucose concentration during the hydrothermal reaction. The surface carbon species evolve with the carbon content and the nitrogen atoms in the structure of carbon nitride are partially substituted by foreign carbon atoms based on XPS measurements. The optimal catalyst leads to the highest H<sub>2</sub>O<sub>2</sub> yield of 1271 μmol L<sup>-1</sup> in an acidic aqueous solution (pH 3) after a reaction period of 4 h, twice higher than the pristine C<sub>3</sub>N<sub>4</sub>. In addition, the largest formation rate constant and the smallest decomposition rate constant of H<sub>2</sub>O<sub>2</sub> are obtained on the optimal one according to the kinetics analyses. The decomposition tests of H<sub>2</sub>O<sub>2</sub> indicate that the formation rate could be a dominant factor impacting the H<sub>2</sub>O<sub>2</sub> yield. The conduction band position of the optimal catalyst is positively shifted to 0.06 V versus RHE, which is more favorable to the reduction of dioxygen to H<sub>2</sub>O<sub>2</sub> (O<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> at 0.69 V versus RHE). The positive shift of valence band also improves hole collection and leads to enhanced formation of H<sub>2</sub>O<sub>2</sub>.

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### 1. Introduction

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), an important and environmentally benign chemical, is not only extensively utilized in a variety of industrial fields but also used in an H<sub>2</sub>O<sub>2</sub>-based fuel cell for generating electric energy [1]. The present industrial production of H<sub>2</sub>O<sub>2</sub> is mainly based on an anthraquinone method, which is highly energy-demanding and accompanied by the generation of undesirable by-products [2]. The direct synthesis of H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub> and O<sub>2</sub> over noble metal catalysts might be an alternative way [3,4]. However, one needs special care to this reaction because the mixture gases of H<sub>2</sub> and O<sub>2</sub> are at a risk to explode in a wide range of concentration ratio. Solar-to-fuel conversion is one of the most promising ways to produce clean energy (e.g. H<sub>2</sub>) and valued chemicals (e.g. H<sub>2</sub>O<sub>2</sub>) and simultaneously to balance the demand of fossil-based fuels [5–11]. Therefore, the solar-driven production

of H<sub>2</sub>O<sub>2</sub> could be a clean, safe and eco-friendly pathway because it involves no pollutant and is free of carbon emission [12].

The key to achieve photosynthesis of H<sub>2</sub>O<sub>2</sub> is to explore efficient, stable and low-cost photocatalysts operated at moderate reaction conditions. TiO<sub>2</sub>, an extensively studied oxide semiconductor, has been used as a catalyst for H<sub>2</sub>O<sub>2</sub> photosynthesis [13,14]. Nevertheless, its wide bandgap (>3 eV) excludes the efficient utilization to the visible light regime of solar spectrum. In addition, the photo-generated holes are capable of decomposing H<sub>2</sub>O<sub>2</sub> on the surface of TiO<sub>2</sub> because of its very positive valence band position (~3.1 V versus RHE), leading to a limited H<sub>2</sub>O<sub>2</sub> yield [15]. Two main strategies have been developed to improve the photocatalytic performance of TiO<sub>2</sub>. One is to load noble metals e.g. Au, Ag and AuAg alloys onto the surface of TiO<sub>2</sub>, which promotes charge separation and suppresses the decomposition of H<sub>2</sub>O<sub>2</sub> [13]. The other is to modify the surface of TiO<sub>2</sub> with appropriate anions [16]. The modification with F-anions greatly enhanced the H<sub>2</sub>O<sub>2</sub> yield possibly because the F-anions block the decomposing pathway of H<sub>2</sub>O<sub>2</sub> on the surface of TiO<sub>2</sub> [17]. Also, the phosphate modification to TiO<sub>2</sub> was proven to effectively diminish the decomposition of H<sub>2</sub>O<sub>2</sub> under the conditions of H<sub>2</sub>O<sub>2</sub> generation [18].

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Besides TiO<sub>2</sub>-based photocatalysts, a new type of C<sub>3</sub>N<sub>3</sub>S<sub>3</sub> polymeric materials was developed for catalyzing H<sub>2</sub>O<sub>2</sub> photosynthesis [19–21]. For example, the Cd<sub>3</sub>(C<sub>3</sub>N<sub>3</sub>S<sub>3</sub>)<sub>2</sub> coordination polymer exhibited impressive photocatalytic H<sub>2</sub>O<sub>2</sub> generation in a methanol/water solution [19]. Another polymeric material with a two-dimensional framework i.e. graphitic phase carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) has also received extensive focus on its activity toward H<sub>2</sub>O<sub>2</sub> photosynthesis due to its appropriate energy levels and visible light response [22–26]. For instance, the g-C<sub>3</sub>N<sub>4</sub> modified with pyromellitic diimide (PDI) units via  $\pi$ - $\pi$  interactions showed a high activity toward H<sub>2</sub>O<sub>2</sub> formation [23]. The modification of PDI led to a positive shift of conduction band of g-C<sub>3</sub>N<sub>4</sub>, enhancing the selectivity to H<sub>2</sub>O<sub>2</sub> by two-electron reduction of dioxygen. Subsequently, the g-C<sub>3</sub>N<sub>4</sub>/PDI/graphene nanohybrid was synthesized and exhibited higher activity owing to the charge-transporting characteristic of graphene [24]. Consequently, it is highly desirable to design C<sub>3</sub>N<sub>4</sub>-based photocatalysts toward H<sub>2</sub>O<sub>2</sub> synthesis because of its metal-free, earth-abundant and easy-made characteristics.

Herein, we reported on a modification strategy to g-C<sub>3</sub>N<sub>4</sub> by content tunable doping of carbon derived from a hydrothermal reaction of glucose to the parent g-C<sub>3</sub>N<sub>4</sub> and subsequent calcination. Such a treatment changes surface carbon species and the electronic structure of g-C<sub>3</sub>N<sub>4</sub>, resulting in a positive shift of its conduction band. The H<sub>2</sub>O<sub>2</sub> yield doubled on the optimal carbon-doped C<sub>3</sub>N<sub>4</sub> in contrast with the pristine C<sub>3</sub>N<sub>4</sub>. The correlations of carbon doping and energy level structure were discussed. The reaction kinetics was studied to determine the formation rate constant and decomposition rate constant of H<sub>2</sub>O<sub>2</sub> over the carbon-doped C<sub>3</sub>N<sub>4</sub> catalysts. This work could pave an efficient and convenient way to surface modification of meta-free g-C<sub>3</sub>N<sub>4</sub> for enhancing the catalytic activity toward H<sub>2</sub>O<sub>2</sub> photosynthesis.

## 2. Experimental

### 2.1. Material and methods

#### 2.1.1. Chemicals

Melamine (1,3,5-triazine-2,4,6-triamine, C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>, 99%), glucose, H<sub>2</sub>SO<sub>4</sub> (sulfuric acid), HClO<sub>4</sub> (perchloric acid), KH<sub>2</sub>PO<sub>4</sub> (potassium dihydrogen phosphate), and K<sub>2</sub>HPO<sub>4</sub>·3H<sub>2</sub>O (potassium hydrogen phosphate, trihydrate), C<sub>3</sub>H<sub>7</sub>OH (Isopropyl alcohol), O<sub>2</sub> (Oxygen, 99.995%), C<sub>2</sub>H<sub>5</sub>OH (Anhydrous ethanol) were purchased from Sinopharm Chemical Reagent (Beijing Co. Ltd.). All reagents were of analytical grade and were used without further purification. Deionized water was used throughout the experiments.

#### 2.1.2. Preparation of graphitic-carbon nitride (g-C<sub>3</sub>N<sub>4</sub>)

The g-C<sub>3</sub>N<sub>4</sub> was prepared by heating of a melamine precursor, similar to the method by Chen et al. [46]. In a typical synthesis, melamine of 3.0 g was placed in a porcelain cup and calcined at 520 °C for 4 h in air with a heating rate of 4 °C min<sup>-1</sup>. Grinding of the product led to light yellow powders.

#### 2.1.3. Preparation of carbon-modified C<sub>3</sub>N<sub>4</sub> (C<sub>3</sub>N<sub>4</sub>-Carbon)

The C<sub>3</sub>N<sub>4</sub> powder was dispersed in an aqueous solution of glucose with varied concentrations and was ultrasonicated for 30 min. The solution was treated in a Teflon-lined autoclave via a hydrothermal reaction at 120 °C for 10 h. The product was centrifuged and washed with deionized water and alcohol 3 times, respectively. Subsequently, the product was dried in an oven at 70 °C for 8 h. The dried product was calcined in an atmosphere of nitrogen gas at 500 °C for 2 h (at a ramping rate of 5 °C min<sup>-1</sup>) to obtain the C<sub>3</sub>N<sub>4</sub>-Carbon (x) powders, where x refers to the initial concentration of glucose in the solution.

### 2.2. Characterizations

HRTEM images were obtained using a JEOL JEM-3010 microscope. For TEM observations, the samples were ultrasonically dispersed in ethanol, and then a drop of the suspension was deposited onto a carbon-coated copper grid followed by evaporation of the solvent in air.

The XRD patterns were collected on a Shimadzu XRD-6000 diffractometer (40 kV, 30 mA, graphite-filtered CuK $\alpha$  radiation,  $\lambda = 0.15418$  nm).

Elemental analyses were performed using a Vairo EL CUBE element analyzer. The XPS spectra were recorded on a Thermo VG ESCALAB MK II X-ray photoelectron spectrometer at a pressure of  $2 \times 10^{-9}$  Pa using Al K $\alpha$  X-ray as the excitation source (1486.6 eV). The positions of all binding energies were calibrated using the C 1s line at 284.8 eV.

Solid-state UV/vis diffuse reflectance spectra were recorded at room temperature using a Shimadzu UV-3000 spectrometer equipped with an integrating sphere attachment using BaSO<sub>4</sub> as background.

Photoluminescence (PL) measurements were conducted on Hitachi F-7000 spectrofluorometer using a laser with an excitation of 400 nm at room temperature.

### 2.3. Photocatalytic formation and decomposition of H<sub>2</sub>O<sub>2</sub>

The catalyst (1 g L<sup>-1</sup>) was dispersed into an aqueous solution with 5 vol% iso-propanol (total volume 30 mL) in a borosilicate glass bottle (diameter of 35 mm, capacity of 50 mL) and was ultrasonicated for 10 min. The pH value of the suspension was tuned to 3 by dropping HClO<sub>4</sub> solution (1 mol L<sup>-1</sup>). The bottle was sealed with a rubber septum cap with a gas inlet and outlet. The solution was first purged by O<sub>2</sub> bubbling while stirring in dark for 30 min. The solution was irradiated using a 300 W Xe lamp at an intensity of 100 mW cm<sup>-2</sup> under stirring. The oxygen purging was continued throughout the reaction. The solution was sample data fixed time to monitor H<sub>2</sub>O<sub>2</sub> concentration. After the first run formation of H<sub>2</sub>O<sub>2</sub> for 240 min, the photocatalyst was removed by centrifugation and was washed thoroughly with water and dried in air. Subsequently, the spent photocatalyst was reused in a fresh solution under the same conditions above. To investigate the decomposition of H<sub>2</sub>O<sub>2</sub> on the catalysts, a catalyst (1 g L<sup>-1</sup>) was dispersed in an acidified H<sub>2</sub>O<sub>2</sub> solution with an initial concentration of 5 mM (pH 3) and irradiated for 90 min under stirring. The concentration of H<sub>2</sub>O<sub>2</sub> was measured based on the method from the literature [47]. The stock solutions of N,N-diethyl-1,4-phenylene-diamine sulfate (DPD), peroxidase (POD) horseradish, and potassium phosphate buffer were prepared as follows. DPD of 0.1 g was dissolved in 10 mL of 0.1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution, and POD of 5 mg was dissolved in water of 5 mL. The POD solution was kept in a refrigerator (4 °C) and was prepared once every 5 days. K<sub>2</sub>HPO<sub>4</sub>·3H<sub>2</sub>O of 1.4 g and KH<sub>2</sub>PO<sub>4</sub> of 6 g were dissolved in water of 100 mL to make a potassium phosphate buffer solution. Aliquots of 2 mL were extracted by a syringe during the reaction at a fixed time and filtered by a 0.45 mm polytetrafluoroethylene (PTFE) filter. Phosphate buffer of 0.8 mL, sample aliquots of 2 mL, DPD of 0.1 mL, POD of 0.1 mL, and water of 2.24 mL were mixed and stirred vigorously for 90 s. Depending on H<sub>2</sub>O<sub>2</sub> concentration generated, the ratio of the sample liquor to water was adjusted to avoid exceeding the detection limit. The calibration curves were plotted according to the range of H<sub>2</sub>O<sub>2</sub> concentrations. The absorbance at 551 nm was monitored using a UV/vis spectrophotometer for quantitative analyses of the concentration.

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