



# Fabrication of platinum-deposited carbon nitride nanotubes by a one-step solvothermal treatment strategy and their efficient visible-light photocatalytic activity



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## ARTICLE INFO

### Article history:

Received 2 August 2014

Received in revised form 9 October 2014

Accepted 14 October 2014

Available online 22 October 2014

### Keywords:

Noble metal

Graphitic carbon nitride

Nanotubes

Hydrogen evolution

Organic pollutant degradation

## ABSTRACT

A series of platinum nanoparticles-deposited carbon nitride nanotubes (Pt/C<sub>3</sub>N<sub>4</sub> NTs) was fabricated by a simple one-step solvothermal treatment strategy using graphite carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) and chloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O) as precursors. The morphology, porosity, phase and chemical structure, and optical and electronic properties of Pt/C<sub>3</sub>N<sub>4</sub> NTs were well characterized. Compared with bulk g-C<sub>3</sub>N<sub>4</sub>, the as-prepared Pt/C<sub>3</sub>N<sub>4</sub> NTs exhibited efficient photocatalytic activity toward hydrogen evolution from water-splitting and aqueous *p*-chlorophenol degradation under visible-light irradiation ( $\lambda > 420$  nm) as a result of their unique tubular nanostructure and the synergic effect of Pt nanoparticles. Subsequently, the activities of simultaneous hydrogen evolution with organic pollutant degradation were also tested using as-prepared Pt/C<sub>3</sub>N<sub>4</sub> NTs under the representative organic pollutants *p*-chlorophenol, *p*-nitrophenol, methylene blue, or rhodamine B as electron donors. Finally, the photocatalytic mechanisms in three different photocatalytic systems were discussed.

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## 1. Introduction

Energy crisis and environmental pollution are two serious problems that humans face in the process of sustainable development [1–3]. In recent decades, the development of semiconductor photocatalytic materials and photocatalytic technique brought new opportunities and challenges for solving the energy and environmental problems [4–7]. Various photocatalytic systems have been widely studied such as hydrogen evolution, organic pollutant degradation, and carbon dioxide reduction [8–10]. Since its discovery in 2008, the application of the visible-light photocatalytic activity of graphite carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) as an effective metal-free semiconductor photocatalyst was extensively developed [11–15]. However, visible-light photocatalytic activity of g-C<sub>3</sub>N<sub>4</sub> is low due to their bulk structure and low quantum efficiency. As such, many researchers were devoted to develop g-C<sub>3</sub>N<sub>4</sub>-based materials with high visible-light photocatalytic activity [16,17]. Nanostructure design and noble metal deposition are two

effective strategies to improve the photocatalytic activity of semiconductor photocatalysts. Therefore, some researchers improved the visible-light photocatalytic activity of g-C<sub>3</sub>N<sub>4</sub> by nanostructure design [18–20]. Because nanostructural g-C<sub>3</sub>N<sub>4</sub> possesses larger number of active sites and exhibits smaller mass transfer resistance in the course of photocatalytic reaction compared with bulk g-C<sub>3</sub>N<sub>4</sub>. Other researchers tried to deposit noble metals on the surface of g-C<sub>3</sub>N<sub>4</sub> for capturing photoexcited electrons, thereby decreasing the photogenerated electron (e<sup>-</sup>)-hole (h<sup>+</sup>) pair recombination probability [21–23]. Unfortunately, some problems exist in the above modification methods: first, the procedure for the nanostructure design is complex and toxic solvents are used in the preparation process. Second, noble metal nanoparticles are directly deposited on the surface of bulk g-C<sub>3</sub>N<sub>4</sub> by traditionally chemical or optical reduction methods; therefore, the electron capturing effect by noble metal nanoparticles is only limited on the surface of bulk g-C<sub>3</sub>N<sub>4</sub>.

In this article, a series of platinum nanoparticles-deposited carbon nitride nanotubes (Pt/C<sub>3</sub>N<sub>4</sub> NTs) were prepared for the first time by a simple one-step solvothermal treatment strategy with Pt nanoparticles uniformly dispersed on the internal and external surface of C<sub>3</sub>N<sub>4</sub> NTs. Ethanol was the lone structure-directing

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agent and reducing agent used in the preparation process. Therefore, the above method for Pt/C<sub>3</sub>N<sub>4</sub> NTs preparation is a real “green” and economic synthesis method. The photocatalytic experiments showed that the visible-light photocatalytic activity of Pt/C<sub>3</sub>N<sub>4</sub> NTs was significantly increased compared with that of bulk g-C<sub>3</sub>N<sub>4</sub> in hydrogen evolution and *p*-chlorophenol degradation system. In addition, the activities of simultaneous hydrogen evolution with organic pollutant degradation were also tested using Pt/C<sub>3</sub>N<sub>4</sub> NTs under representative organic pollutants (OPs) *p*-chlorophenol (PCP), *p*-nitrophenol (PNP), methylene blue (MB), or rhodamine B (RB) as electron donor conditions. Both hydrogen evolution and organic pollutant degradation reactions are based on the same photo-induced charge transfer process. However, the above photocatalytic reactions are performed usually by different photocatalysts under different experimental conditions because of the difference in their required charge transfer characteristics [24]; the organic pollutant degradation reaction originates from single-electron transfer under aerobic conditions whereas hydrogen evolution reaction is carried out by two-electron transfer in the absence of oxygen. Some organic pollutants of which redox potential is more negative than the valence band (VB) potential of TiO<sub>2</sub> can be used as an electron donor for hydrogen evolution reaction. So far, the photocatalytic system on simultaneous hydrogen evolution with organic pollutant degradation has been investigated by some researchers using TiO<sub>2</sub>-based photocatalysts [25,26]. However, this special photocatalytic system has never been studied by using g-C<sub>3</sub>N<sub>4</sub>-based photocatalysts.

## 2. Experimental

### 2.1. Chemicals and reagents

Melamine (C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>, AR grade) was purchased from Tianjin Damao Chemical Reagent. Chloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, GR grade) was purchased from Sinopharm Chemical Reagent Co. Ltd. Triethylamine ((C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N, AR grade, abbreviated TEA) was purchased from Shanghai Fine Chemical Technology Co. Ltd. *p*-Chlorophenol (C<sub>6</sub>H<sub>5</sub>ClO, GC grade, abbreviated PCP), *p*-nitrophenol (C<sub>6</sub>H<sub>5</sub>NO<sub>3</sub>, GC grade, abbreviated PNP), methylene blue (C<sub>16</sub>H<sub>18</sub>ClN<sub>3</sub>S·3H<sub>2</sub>O, HPLC grade, abbreviated MB), and rhodamine B (C<sub>28</sub>H<sub>31</sub>ClN<sub>2</sub>O<sub>3</sub>, HPLC grade, abbreviated RB) were purchased from Aladdin Chemistry Co. Ltd. All chemicals were used without further purification. Double distilled water was used in the catalyst preparation and subsequent catalytic tests.

### 2.2. Preparation of Pt/C<sub>3</sub>N<sub>4</sub> NTs by one-step solvothermal treatment

Pure g-C<sub>3</sub>N<sub>4</sub> sample was prepared by directly calcining melamine in air. Typically, 50 g of melamine powder was put into a 100 mL alumina crucible with a cover. The crucible was heated to 250 °C from room temperature in a muffle furnace at a heating rate of 5 °C/min, and then continued heated to 550 °C at a heating rate of 10 °C/min. Keeping the temperature at 550 °C for 2 h, the yellow g-C<sub>3</sub>N<sub>4</sub> sample was obtained after natural cooling.

Pt/C<sub>3</sub>N<sub>4</sub> NTs was fabricated by one-step solvothermal treatment, with g-C<sub>3</sub>N<sub>4</sub> and H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O as precursors. First, 1 g of g-C<sub>3</sub>N<sub>4</sub> powder was uniformly dispersed into 15 mL ethanol using a 500 W ultrasonic crusher for 1 h. Subsequently, the desired amount of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (26.6, 53.2, 79.8, and 106.4 mg) was dissolved in 15 mL ethanol. The above H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O/ethanol solution was successively added in the above g-C<sub>3</sub>N<sub>4</sub>/ethanol suspension. After stirring the resulting mixture for 1 h at room temperature, the mixture was subject to solvothermal treatment at 150 °C for 24 h at a heat rate of 1 °C/min. The final products were obtained by drying

at 60 °C for 24 h and thermal treatment at 120 °C for 24 h, respectively, and denoted as Pt(x%)/C<sub>3</sub>N<sub>4</sub> NTs, where x% represents Pt nanoparticles deposited mass percentage in the products.

For comparison, C<sub>3</sub>N<sub>4</sub> NTs and Pt(2%)/TiO<sub>2</sub> samples were also prepared by the same method but in the absence of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O precursor and use TiO<sub>2</sub> as a support. Pure TiO<sub>2</sub> was prepared by traditional sol-gel method and crystallizing at 450 °C for 5 h.

### 2.3. Characterizations

Transmission electron microscopy (TEM) images were recorded on a JEOL JEM-2010 transmission electron microscope at an accelerating voltage of 200 kV. Field emission scanning electron microscopy (FESEM) images were recorded using a Nova NanoSEM450 field emission scanning electron microscope. The chemical compositions and elemental mappings of the samples were determined by energy-dispersive X-ray spectrometer (EDX) equipped on FESEM. Nitrogen gas porosimetry measurements were performed on a Quantachrome NOVA 2000e surface area and porosity analyzer after the samples were outgassed under a vacuum at 70 °C for 20 min and 150 °C for 6 h. X-ray diffraction (XRD) patterns were obtained using a Panalytical X'Pert PRO diffractometer via Cu Kα radiation. Fourier transform infrared (FTIR) spectra were recorded on a Bruker VERTEX 70 FTIR apparatus. X-ray photoelectron spectra (XPS) was performed using a VG-ADES 400 instrument with an Mg Kα-ADES source at a residual gas pressure of less than 10<sup>-8</sup> Pa. UV-visible/diffuse reflectance spectroscopy (UV-vis/DRS) was conducted using a Lambda 750S UV/VIS/NIR spectrometer. Photoluminescence (PL) measurements were carried out on a HITACHI F-7000 fluorescence spectrophotometer.

### 2.4. Photocurrent measurements

Photocurrent measurements were carried out using the conventional three electrode setup connected to an electrochemical station (CHI 630E, Shanghai Chenhua, China). In this electrochemical system, the prepared catalyst/Ti sheet was used as the working electrode; a Pt wire was used as the counter electrode and an Ag/AgCl electrode (saturated KCl) was used as the reference electrode. The electrolyte was 0.01 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> aqueous solution (100 mL). A 300 W Xe lamp served as a light source. The measurements were carried out at a constant potential of +1.0V to the working electrode.

### 2.5. Photocatalytic tests

#### 2.5.1. Hydrogen evolution by using TEA as an electron donor

A PLS-SXE300 Xe lamp (300 W, Beijing PerfectLight Co. Ltd., China) served as the light source, and the output wavelength λ > 320 nm. The visible light irradiation was obtained by removing the UV irradiation from the lamp using a 420 nm cut filter, which can control the output wavelength λ > 420 nm. 100 mg of solid catalyst loaded with 3 wt% of Pt co-catalyst (for bulk g-C<sub>3</sub>N<sub>4</sub> and C<sub>3</sub>N<sub>4</sub> NTs only) and 100 ml of H<sub>2</sub>O containing 10 vol% TEA were poured into a 300 mL quartz reactor. The above suspension was ultrasonicated for 10 min and stirred in dark for 1 h. Subsequently, the light source was switched on, and further stirring was applied. The temperature of the suspension was maintained at 35 ± 2 °C by circulation of water through an external cooling jacket. The generated hydrogen was *in situ* analyzed with a GC 7890-II TCD gas chromatograph (TECHCOMP) using an MS-5 A column, which was connected to the gas circulating line with argon carrier.

#### 2.5.2. Photocatalytic degradation of aqueous PCP

100 mg of solid catalyst and 100 mL of PCP aqueous solution was poured into a 300 mL self-designed quartz reactor. The initial

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