



Contents lists available at ScienceDirect

Catalysis Today

journal homepage: [www.elsevier.com/locate/cattod](http://www.elsevier.com/locate/cattod)

## 2D/1D heterostructure of g-C<sub>3</sub>N<sub>4</sub> nanosheets/CdS nanowires as effective photo-activated support for photoelectrocatalytic oxidation of methanol

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### ARTICLE INFO

#### Keywords:

Graphitic carbon nitride  
Cadmium sulfide  
Photo-activated support  
Methanol oxidation  
Visible light

### ABSTRACT

In this paper, Pt nanoclusters are firstly decorated on the surface of two dimensional (2D) g-C<sub>3</sub>N<sub>4</sub> nanosheets. Furthermore, 1D CdS nanowires are introduced to form the heterojunction of g-C<sub>3</sub>N<sub>4</sub>/CdS. The as-prepared Pt/g-C<sub>3</sub>N<sub>4</sub>/CdS shows 7.4 times improved electrocatalytic performance on methanol oxidation under visible light (> 420 nm) irradiation compare to dark condition. Moreover, the stability of corresponding electrode is significantly improved by evaluating on chronoamperometric and chronopotentiometry curves. The synergistic effects of photo- and electro-catalysis together with the efficient charger separation in the heterojunction of g-C<sub>3</sub>N<sub>4</sub>/CdS contribute to the above improvements. The present studies provide an effective pathway to design a heterojunction as the photo-activated support in the application of direct methanol fuel cell.

### 1. Introduction

Direct methanol fuel cells (DMFCs) have been recognized as promising future power sources because of their environmental benignity, rapid recharging, and high energy density, *etc.* [1–4]. The anodic oxidation of fuels *via* an electrocatalyst is a key reaction in the DMFCs. However, traditional electrocatalysts (*viz.* Pt) suffer from high-cost and easily to be poisoned by intermediate species (CO), which hamper the further commercialization of DMFCs [2–4]. Recently, photo-activated semiconductors as supports to improve the electrocatalytic performance of methanol oxidation have been attracted great interesting [5–18]. This is because that the selection of support resulting in better dispersion and lower loading amount of Pt. More importantly, the semiconductor nanostructures have strong photocatalytic activity under light irradiation. It can be excited when the light energy is higher than its band gap, resulting in photogenerated electron-hole pairs and then participating the redox reactions [5–18].

Two dimensional (2D) graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>), as a typical polymeric semiconductor, has been used in the various photocatalytic applications, including hydrogen and oxygen production from water, pollutants degradation, and organic photosynthesis, *etc.* [19–23]. Because of its visible-light response, high thermal and chemical stability,

abundance, and nontoxic nature, g-C<sub>3</sub>N<sub>4</sub> was considered to be one of the most promising photocatalyst. Moreover, the nitrogen rich polymeric semiconductors structurally in the carbon nitride matrix endows with g-C<sub>3</sub>N<sub>4</sub> abundant reactive sites for the hybridization with other components. For example, in our previous research, g-C<sub>3</sub>N<sub>4</sub> nanosheet was used as a photo-activated support for the deposition of ultrasmall Pt nanoclusters [14]. Under visible light irradiation, the as-prepared Pt/g-C<sub>3</sub>N<sub>4</sub> composite showed 3.3 and 1.9 folds enhanced catalytic activity for the oxidation of methanol in alkaline and acid medium, respectively, compared to ambient reaction. However, the rapid recombination of photo-generated electron–hole pairs and relative absorption in the visible light region (< 460 nm) in the pure g-C<sub>3</sub>N<sub>4</sub> restrict its broadly applications.

One dimensional (1D) cadmium sulfide (CdS) nanostructure with its unique and versatile fundamental properties including narrow bandgap (2.4 eV), excellent transport properties, and high electronic mobility, *etc.*, has been received great attraction [24,25]. We known that the conduction band (CB) and valance band (VB) potentials of g-C<sub>3</sub>N<sub>4</sub> and CdS are about –1.13 and –0.5 eV, and 1.57 and 1.88 eV, respectively, according to the reported results [26,27]. Based on their band structures diagram, a type II heterojunction can be formed by the construction of g-C<sub>3</sub>N<sub>4</sub> and CdS, resulting in efficient separation of

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<https://doi.org/10.1016/j.cattod.2018.02.043>

Received 7 November 2017; Received in revised form 15 February 2018; Accepted 23 February 2018

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photogenerated charge carriers and consequently improving photocatalytic performance. Accordingly, various g-C<sub>3</sub>N<sub>4</sub>/CdS hybrids were fabricated and used as effective photocatalysts [26–33]. However, most of above investigations focused on CdS nanoparticles and used for the photocatalytic degradation of dyes or H<sub>2</sub> production [26–29,30–33], while few reports have been reported on 2D g-C<sub>3</sub>N<sub>4</sub> hybridized with 1D CdS and further extend to other applications.

Accordingly, it is strongly desirable to explore the potential photoelectrocatalytic oxidation of methanol of 2D/1D g-C<sub>3</sub>N<sub>4</sub>/CdS as a photo-activated support for traditional Pt electrocatalyst. Herein, ultrasmall Pt nanoclusters were decorated on the surface of 2D g-C<sub>3</sub>N<sub>4</sub> nanosheets firstly. Furthermore, 1D CdS nanowires were hybridized with as-prepared Pt/g-C<sub>3</sub>N<sub>4</sub> to form the composites of Pt/g-C<sub>3</sub>N<sub>4</sub>/CdS. Finally, the as-prepared Pt/g-C<sub>3</sub>N<sub>4</sub>/CdS electrode showed much higher photoelectrocatalytic performance (7.4 times) towards methanol oxidation with assistance of visible light irradiation compare to ambient reaction. The synergistic effect of photocatalytic and electrocatalytic process is demonstrated in the process of catalytic oxidation of methanol. Moreover, compared to Pt/g-C<sub>3</sub>N<sub>4</sub>, the introduced CdS nanowires improved the catalytic activity (1.4 times) and the stability of electrodes under visible light irradiation. The efficient interfacial charge transfer in the heterojunction of g-C<sub>3</sub>N<sub>4</sub>/CdS contributes to the enhanced photoelectrocatalytic performance.

## 2. Experimental section

### 2.1. Materials and characterization

Chloroplatinic acid hexahydrate (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O), thiourea (CH<sub>4</sub>N<sub>2</sub>S), cadmium acetate dehydrate (C<sub>4</sub>H<sub>6</sub>CdO<sub>4</sub>·2H<sub>2</sub>O), ethylenediamine (C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>), potassium hydroxide (KOH), and methanol (CH<sub>3</sub>OH) were purchased from Sinopharm Chemical Reagent Co., Ltd. without purification in advance. High-purity deionized water was used throughout the studies.

### 2.2. Synthesis of g-C<sub>3</sub>N<sub>4</sub> nanosheets and Pt/g-C<sub>3</sub>N<sub>4</sub> nanocomposites

The g-C<sub>3</sub>N<sub>4</sub> nanosheets were prepared by heating urea in the semiclosed system, as reported in our previous works [14].

The Pt/g-C<sub>3</sub>N<sub>4</sub> nanocomposites were synthesized by a hydrothermal method. Basically, 20 mg g-C<sub>3</sub>N<sub>4</sub> and 0.68 mL H<sub>2</sub>PtCl<sub>6</sub> (3.8 × 10<sup>-2</sup> M) were added into 20 mL ethanol and water mixture solution (V<sub>ethanol</sub>:V<sub>water</sub> = 1:1) and then with ultrasonication for 30 min. Then, the above mixture solution was transferred into 25 mL Teflon autoclave and held at 140 °C for 4 h. After reaction, the temperature of Teflon autoclave was cooled to room temperature naturally, and the powders were collected by centrifugation and washed with water and ethanol thoroughly. Finally, the powders were dried at 50 °C in vacuum oven overnight, resulting in Pt decorated on the surface of g-C<sub>3</sub>N<sub>4</sub> nanosheets (Pt loading amount is ca. 20 wt%).

### 2.3. Synthesis of CdS nanowires, g-C<sub>3</sub>N<sub>4</sub>/CdS and Pt/g-C<sub>3</sub>N<sub>4</sub>/CdS nanocomposites

The CdS nanowires were synthesized by a solvothermal method [34]. C<sub>4</sub>H<sub>6</sub>CdO<sub>4</sub>·2H<sub>2</sub>O (0.30 g) and CH<sub>4</sub>N<sub>2</sub>S (0.28 g) were dispersed in 20 mL C<sub>2</sub>H<sub>8</sub>N<sub>2</sub> under ultrasonication with 1 h. Then, the mixture solution was transferred into a Teflon autoclave (25 mL) and held at 180 °C for 72 h. After the temperature of Teflon autoclave was cooled to room temperature naturally, yellow powders were collected by centrifugation and washed with ethanol and water drastically. Then, the samples were dried in vacuum oven at 60 °C overnight.

The g-C<sub>3</sub>N<sub>4</sub>/CdS heterojunction were prepared by a physical mixing method under ultrasonication. Typically, 16 mg as-prepared g-C<sub>3</sub>N<sub>4</sub> and 4 mg CdS were added into 20 mL water under ultrasonication with 1 h, and then kept stirring overnight. The samples were collected by

centrifugation and washed by water and ethanol thoroughly, resulting in g-C<sub>3</sub>N<sub>4</sub>/CdS heterojunction. The amount of CdS accounts for 20% of the total mass in this procedure. The corresponding Pt/g-C<sub>3</sub>N<sub>4</sub>/CdS nanocomposites were prepared by same method except that the g-C<sub>3</sub>N<sub>4</sub> was instead of Pt/g-C<sub>3</sub>N<sub>4</sub>.

### 2.4. Preparation of working electrode

For electrocatalytic and photoelectrocatalytic oxidation of methanol: Pt/g-C<sub>3</sub>N<sub>4</sub> or Pt/g-C<sub>3</sub>N<sub>4</sub>/CdS modified electrode as working electrode were prepared as follow: 2 mg samples and 10 μL Nafion (Dupond, USA) solution were added into 1 mL ethanol/water mixture solution (V<sub>ethanol</sub>: V<sub>water</sub> = 1:1) under ultrasonication for 30 min to form an homogeneous dispersion. After that, 5 μL of well dispersed catalyst ink was deposited on a pre-polished glassy carbon electrode (GCE, 3 mm diameter) surface and dried in air at room temperature.

For photoelectrocatalytic degradation of methyl blue (MB), 100 mg of g-C<sub>3</sub>N<sub>4</sub> or g-C<sub>3</sub>N<sub>4</sub>/CdS samples and 20 μL of Nafion were added into 1 mL of ethanol/water mixture solution with ultrasonication for 30 min to obtain a homogeneous dispersion, respectively. And then, 100 μL of the above dispersion was dropped on the surface of F-doped tin oxide (FTO, 1.0 cm × 1.0 cm), and dried in air at room temperature.

### 2.5. Electrochemical and photoelectrochemical measurements

The electrochemical and photoelectrochemical (PEC) measurements were carried out in the quartz beaker via an electrochemical workstation CHI 660E (Shanghai Chenhua Instrumental Co., Ltd., China) with three electrodes system, wherein the Pt/g-C<sub>3</sub>N<sub>4</sub>/CdS or Pt/g-C<sub>3</sub>N<sub>4</sub> modified electrode was acted as working electrode. Pt wire and saturated calomel electrode (SCE) were acted as counter and reference electrodes, respectively. Cyclic voltammeteries (CVs) of the working electrodes were monitored in 1.0 M CH<sub>3</sub>OH and 1.0 M KOH solution in the range of -0.7 to 0.2 V (vs. SCE). The chronoamperometry (CA) and chronopotentiometry (CP) of the working electrode with or without visible light irradiation in 1.0 M CH<sub>3</sub>OH and 1.0 M KOH solution were recorded at a potential of -0.2 V and 20 μA, respectively. Electrochemical impedance spectroscopy (EIS) measurements were carried out by using 2.5 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>]/K<sub>4</sub>[Fe(CN)<sub>6</sub>] (1:1) mixture as a redox probe in 0.1 M KCl solution. The EIS spectra were recorded under an AC perturbation signal of 5.0 mV over the frequency range from 100 kHz to 0.1 Hz at a potential of 0.2 V (vs. SCE). Linear sweep voltammetry (LSV) of the working electrode was tested in 1.0 M CH<sub>3</sub>OH and 1.0 M KOH solution in the range of -0.7 to -0.2 V (vs. SCE).

The photoelectrocatalytic degradation of MB: g-C<sub>3</sub>N<sub>4</sub>/CdS modified electrode was immersed in 20 mL of MB aqueous solution (5 mg L<sup>-1</sup>) with 0.6 V bias potential and the working electrode was irradiated by using a Xe arc lamp (150 W) equipped with UV cut-off filter (> 420 nm). Before experiments were carried out, the system was kept for 5 h in a dark room to achieve an equilibrium adsorption state. The integrated visible-light intensity was measured to be ca. 54 mW cm<sup>-2</sup>.

### 2.6. Characterization

The samples were characterized using transmission electron microscopy (TEM, JEOL, 2100, operated at 100 kV), and HAADF-STEM-EDX (JEM-3000F, operated at 300 kV). Scanning electron microscope (SEM, JEOL, JSM-6330FT) was used for morphology characterization, and the attached energy dispersive X-ray (EDX) was used for elemental detection. UV-VIS-NIR Shimadzu UV3150 spectrophotometer (Japan) was employed for the UV-vis diffuse reflectance spectra measurements. A PANalytical X'Pert PRO MRD system with Cu Kα radiation (k = 1.54056 Å) operated at 40 kV and 30 mA was used to obtain X-ray diffraction (XRD) patterns of the samples. X-ray photoelectron spectroscopy (XPS) was conducted on an ESCALab220i-XL electron spectrometer. The binding energies were referenced to the C 1s line at

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