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# Carbon dots decorated graphitic carbon nitride as an efficient metal-free photocatalyst for phenol degradation

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ABSTRACT

Environment-friendly metal-free photocatalysts represent a promising alternative to conventional metal-based semiconductors. In this report, a carbon dots (CDs) decorated graphitic carbon nitride (g-$C_3N_4$) photocatalyst was synthesized via a facile impregnation-thermal method. Under visible light irradiation, a very low CDs content of 0.5 wt% in the g-$C_3N_4$/CDs composite resulted in a 3.7 times faster reaction rate for phenol photodegradation than pristine g-$C_3N_4$. Spectroscopic and photoelectrochemical characterizations revealed that impregnation of CDs into g-$C_3N_4$ not only enhanced the production of photogenerated electron-hole pairs by extending the visible light absorption region due to the upconverted photoluminescence character of CDs, but also facilitated electron-hole separation by band alignment in the g-$C_3N_4$/CDs junction, thus yielded more holes, $^{\bullet}O_2^{-}$ and $^{\bullet}OH$ radicals to promote phenol degradation. These results highlight the potential application of sustainable metal-free photocatalysts in water purification.

## 1. Introduction

Sunlight-driven photocatalytic reactions represent a promising way to address the increasing environmental and energy concerns [1–4]. From the viewpoint of solar-energy use, photocatalytic performance strongly depends on the semiconductor's absorption capacity toward sunlight and the reaction efficiency of photogenerated charge carriers. To date, various visible-light-sensitive semiconductors, including multi-metal oxides, sulfides and oxynitrides, have been successfully fabricated by band-structure engineering [5–8]. Nevertheless, considering the side issues such as scalability and sustainability, earth-abundant metal-free semiconductors are greatly desired. As a sustainable material, graphitic carbon nitride (g-$C_3N_4$) represents an attractive visible light photocatalyst because of its suitable band gap (2.7 eV) for sunlight absorption and outstanding catalytic activity [9]. The high chemical stability of g-$C_3N_4$ together with the low cost of mass production makes it an ideal candidate for applications like photocatalytic water splitting, $CO_2$ reduction and pollutant degradation [10–14]. However, despite great progress in g-$C_3N_4$ synthesis, the weak van der Waals interactions between adjacent CN layers in g-$C_3N_4$ impede charge transfer and separation, and thus impose severe limitations on the photocatalytic performance.

One promising strategy to enhance the photocatalytic performance of g-$C_3N_4$ is to form surface junctions to promote charge separation. Two typical approaches have been developed to construct effective surface junctions. One is to decorate g-$C_3N_4$ with metal nanoparticles (e.g., Au and Ag) or carbon nanomaterials (e.g., carbon nanotube and graphene), which can effectively capture photogenerated electrons in g-$C_3N_4$ and improve catalytic efficiency [15–18]. The other promising approach is to construct semiconductor heterojunctions with a suitable band- alignment structure, such as CdS and $Cu_2O$ [19–23] . Such structures can simultaneously optimize light capture and facilitate charge separation at the interface between the two semiconductors. It is noted that the formation of effective junctions strongly depends on the crystal structure, band structure, electron affinity and interfacial contact of both materials. However, the main problem of these composites is the leaching of toxic metals during photocatalytic processes. Photocatalytic systems based on metal-free, sustainable materials are highly desirable for large-scale photocatalytic applications.

Recently, carbon dots (CDs), which are predominantly composed of graphitic carbon ($sp^2$ carbon) with a size below 10 nm, have attracted considerable attention because of their unique optical and electronic properties [24,25]. The quantum effect endows CDs with broad-band optical absorption. Thus, CDs have been

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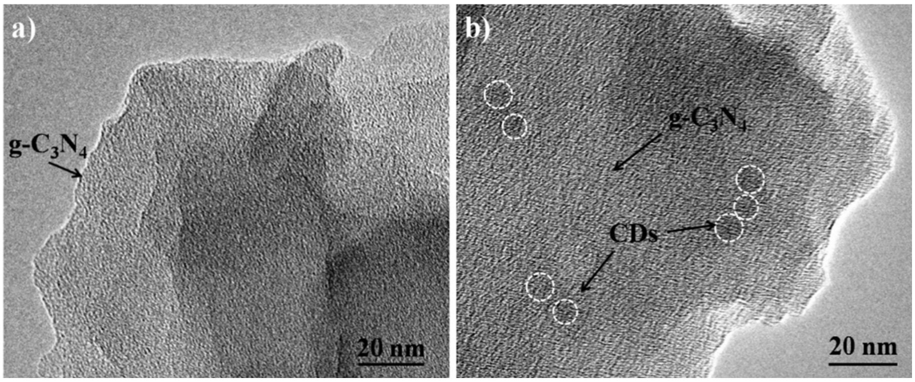

**Fig. 1.** TEM images of (a) g-$C_3N_4$ and (b) g-$C_3N_4$/CDs (0.5 wt%) composite.

widely used as light absorbers to couple with semiconductor nanoparticles, such as $TiO_2$, Si and $Ag_3PO_4$, to improve their photocatalytic performance [26–28]. In addition, CDs also act as an electron acceptor or transporter to direct the flow of photogenerated charge carriers [29] . Considering the analogous $\pi$−conjugated structure of g-$C_3N_4$ and CDs, the combination of these two materials is expected to deliver high photocatalytic performance.

With the above merits, we report an earth-abundant, metal-free g-$C_3N_4$/CDs heterojunction synthesized by directly coating CDs onto the g-$C_3N_4$ surface. The CDs decorated g-$C_3N_4$ composite exhibited greatly enhanced photocatalytic activity toward phenol degradation under visible light irradiation compared with that of g-$C_3N_4$. The role of the CDs in the composite was systemically investigated. The metal-free and environment-friendly properties of the g-$C_3N_4$/CDs composite make it a promising photocatalytic system for practical applications.

## 2. Experimental

### 2.1. Chemicals and materials

Cyanamide was purchased from Alfa Aesar (Ward Hill, MA, USA). Phenol was purchased from Sigma- Aldrich (St. Louis, MO, USA). 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO) was obtained from Dojindo Laboratories (Kumamoto, Japan). Methanol was obtained from Fisher Scientific (Pittsburgh, PA, USA). All other chemicals were of analytical grade and used without further purification. All solutions were freshly prepared with deionized water (resistivity: 18.2 MΩ) obtained using a Millipore Milli-Q water purification system (Bedford, MA, USA).

### 2.2. Synthesis of g-$C_3N_4$

Pure g-$C_3N_4$ was prepared by a simple calcination method according to the literature [30]. Cyanamide was put into a quartz boat and heated in static air to 520 °C (ramp rate: 2 °C/min) and then kept for 4 h. The yellow g-$C_3N_4$ product was collected and ground into powder with an agate mortar for further use.

### 2.2.1. Synthesis of g-$C_3N_4$/CDs nanocomposite

CDs were synthesized by the pyrolysis of citric acid and branched poly(ethylenimine) according to our previous report [31]. A typical preparation of g-$C_3N_4$/CDs nanocomposite was as follows: g-$C_3N_4$ (0.2 g) and a certain volume of CDs aqueous solution (1 mg $mL^{-1}$) were mixed and vigorously stirred for 24 h, followed by vaporizing the solvent at 100 °C in an electric thermostatic drying oven. The as-obtained powder was calcined at 300 °C for 1 h at ambient conditions. Following the same procedure, different mass ratios of g-$C_3N_4$/CDs nanocomposites with 0.1 wt%, 0.2 wt%, 0.5 wt% and 1 wt% CDs, respectively, were synthesized.

### 2.3. Characterization

The morphology of the synthesized photocatalysts was examined by transmission electron microscopy (TEM) using a JEOL 2100F instrument (Tokyo, Japan) operated at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) data were obtained on a Thermo VG ESCALAB 250 spectrometer (East Grinsted, UK) with Al Kα radiation at 1486.6 eV. Fourier transform infrared (FTIR) spectra were recorded on a JASCO 6100 spectrophotometer (Japan). UV–vis diffuse reflectance measurements were performed on a Varian Cary 5000 spectrometer (Palo Alto, CA, USA). Fluorescence spectra were obtained on a Horiba Fluoromax-4spectrofluorimeter (Edison, NJ, USA). The total organic carbon (TOC) was measured using a multi N/C 3000 analyzer (Analytik Jena AG, Germany). Electron spin resonance (ESR) signal of radicals spin-trapped by DMPO was recorded on a Bruker ER073 spectrometer (Karlsruhe, Germany) during visible light irradiation of the suspension (0.05 mg $mL^{-1}$ photocatalyst, 100 mM DMPO). The settings for ESR measurements were as follows: center field 3503.95 G, microwave frequency 9.84 GHz, and power 20 mW. Photoelectrochemical measurements were performed in a three-electrode quartz cell on a CHI 630B electrochemical workstation (Shanghai, China). A Pt plate and Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. The working electrodes were prepared by spreading a slurry of the as-prepared photocatalyst onto the fluorine-doped tin oxide (FTO) glass. Photocurrent-time curves were measured in 0.1 M $Na_2SO_4$ electrolyte. Electrochemical impedance spectra (EIS) were measured in 0.1 M KCl solution containing 2.5 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1:1) with a sinusoidal ac perturbation of 5 mV over a frequency range of 1 MHz to 100 mHz.

### 2.4. Photocatalytic performance evaluation

Photodegradation of a phenol solution (10 mg $L^{-1}$) was performed to evaluate the photocatalytic performance of the synthesized catalysts, which was carried out in a top-window Pyrex cell with the temperature maintained at 20 °C by a circulating water system. The catalyst (50 mg) was added into the phenol solution (50 mL). Prior to irradiation, the suspension was magnetically stirred in the dark for 30 min to ensure phenol adsorption/desorption equilibrium. Then, the suspension was irradiated by a 300 W Xe lamp with a cut off filter (<400 nm) and an irradiation intensity of 100 mW $cm^{-2}$. At given time intervals, aliquots of the irradiated suspension were collected, centrifuged and analyzed on an Aligent 1260 high-performance liquid chromatography (HPLC) (Palo Alto, CA, USA) with a Poroshell 120 EC-C18 column.