

Mesoporous graphitic carbon nitride as photo-catalyst for oxidative desulfurization with oxygen



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ABSTRACT

In this study, we present a simple but efficient photocatalyst of mesoporous graphitic carbon nitride (mpg-C₃N₄) that can activate molecular O₂ to oxidize dibenzothiophene under visible light. The desulfurization rate of the simulated oil was 100% under optimal conditions at room temperature. Mpg-C₃N₄ is characterized using transmission electron microscopy, nitrogen adsorption–desorption isotherm, and X-ray diffraction.

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1. Introduction

Given the serious problem of pollution in the environment, deep desulfurization of fuel oil has attracted much attention by investigators. Hydrodesulfurization (HDS) is widely adapted to the desulfurization process in the industry. However, HDS is operated under high temperature and pressure, thereby causing a waste of energy in the production of clean fuel oil.

In the past decades, several non-HDS methods such as adsorptive desulfurization, biodesulfurization, extraction desulfurization, and oxidative desulfurization (ODS) have been utilized to achieve ultra-deep desulfurization [1–4]. Among the abovementioned methods, ODS is one of the most promising strategies for ultra-deep desulfurization of fuel oil because of its mild operating conditions and high efficiency [5]. In the ODS process, hydrogen peroxide (H₂O₂) is generally used as an oxidant to oxidize sulfur-containing compounds to the corresponding sulfone. Sulfone is then extracted out of the oil using an extraction agent [6,7]. However, H₂O₂ production, storage, and application are dangerous and are potential obstacles for the oxidative desulfurization technology with H₂O₂ as an oxidant in industrial applications. Oxygen may be a good choice as an oxidant because of its abundance in nature and because it is not dangerous under mild pressure conditions. Li et al. [8] performed ODS with [C₁₈H₃₇N(CH₃)₃]₅PV₂Mo₁₀O₄₀ as the catalyst

and the oxygen molecule as the oxidant; the desulfurization rate reached up to 100% under mild reaction conditions. Wang et al. also reported the application of [Bmim]BF₄ as the ODS catalyst with the oxygen molecule as the oxidant [9]. However, these ODS methods used the homogeneous catalyst as the oxidant, thereby leading to the difficulty of separating products and catalysts. Therefore, developing an ODS process with the heterogeneous catalyst and the oxygen molecule as the oxidant is significant.

Carbon nitride (C₃N₄) is typically used for hydrogen generation, dye degradation, CO₂ reduction, and other fields under visible light conditions [10–17]. However, one drawback of C₃N₄ as the ODS catalyst is its very low specific surface area (about 14.9 m²/g) [18]. In our previous work [19], C₃N₄ with high specific surface area has been carried out as the support of heteropolyacid, and the obtained catalyst displays excellent recycle ability in ODS process. In that paper, C₃N₄ is only used as the support, and the active component for ODS is heteropolyacid. However, as a well known photocatalyst, the band gap of C₃N₄ is 2.7 eV, and the position of the conduction band (CB) and valence band (VB) is situated at −1.3 V and 1.4 V versus the normal hydrogen electrode (NHE) (E°), respectively [20]. The electrons that are excited by visible light of CB have a remarkable capacity to reduce O₂ (E°(O₂/•O₂[−]) = −0.16) and form a strong oxidizing superoxide radical anion (•O₂[−]). N-containing C₃N₄ can reductively adsorb O₂ in principle [21]. Based on the literature results, we infer that C₃N₄ may be used as photocatalyst for ODS process.

In this paper, mpg-C₃N₄ is synthesized and extensively characterized using transmission electron microscopy (TEM), X-ray diffraction (XRD), and nitrogen adsorption–desorption isotherm. The obtained (mpg-

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C₃N₄) is used as photocatalyst for ODS process under visible light condition.

2. Experimental

2.1. Materials

NH₄HF₂ (98%) and DBT (99%) were supplied by the J&K Scientific Company. Benzothiophene (BT, 97%) and 4,6-dimethylbenzothiophene (4,6-DMDBT, 99%) were purchased from Aladdin. Cyanamide was bought from Adamas Reagent Co., Ltd. LUDOX HS-40 colloidal silica (40 wt.%) was supplied by Sigma–Aldrich and all chemicals used were obtained from commercial sources.

2.2. Catalyst synthesis

The mpg-C₃N₄ was prepared according to previous reports [22]. Cyanamide (5 g) was dissolved in silica sol (12.5 g, 40% dispersion of 12 nm SiO₂ particles) with stirring at 60 °C overnight. The obtained mixtures were placed in the tube furnace, heated at 2.3 °C min⁻¹ rate to reach 500 °C, and were kept at this temperature for 4 h. The brown-yellow product was added to 4 M of NH₄HF₂ solution to remove the silica template for 2 days, after which washing was performed with distilled water and ethanol. Finally, the mpg-C₃N₄ was obtained by drying it at 100 °C under vacuum overnight. Dicyandiamine was calcined 2.3 °C min⁻¹ rate to reach 500 °C and was kept at this temperature for 4 h. The obtained yellow sample is C₃N₄ [22].

2.3. Characterization

XRD patterns were collected on a Rigaku D/MAX-3B powder X-ray diffractometer using the Cu K α radiation ($k = 0.15418$ nm). Brunauer–Emmett–Teller (BET) surface area analysis was measured by the Micromeritics Model ASAP 2020 instrument. The pore volume and average pore diameter were calculated based on the Barrett–Joyner–Halenda method. TEM measurements were conducted via a Tecnai G² F20 S-TWIN microscope at an accelerating voltage of 200 kV. FT-IR spectra were obtained using a Nicolet FT-IR spectrophotometer (Nexus 470, Thermo Electron Corporation) with pressed KBr pellets.

2.4. Photocatalytic oxidative desulfurization

DBT, 4,6-DMDBT, and BT were dissolved in n-octane with 100 ppmw to prepare the model fuel, respectively. The reaction system was performed under constant stirring using O₂ in a closed glass vessel (100 ml) containing 10 ml of model fuel and 0.1 g mpg-C₃N₄ at room temperature with visible light. The mixtures were stirred for 30 min in the dark to achieve adsorption–desorption equilibrium before irradiation. The mixtures were then irradiated by 300 W xenon lamp (visible light). The oxidized DBT was extracted using methanol, and the clarified model fuel after the reaction was detected using a microcoulometric detector (WK-2D). The recycled catalyst was filtrated and washed with methanol.

3. Results and discussion

The XRD pattern of mpg-C₃N₄ is shown in Fig. S1A, which shows a strong diffraction peak at 27.4° corresponding to a (002) diffraction plane. The diffraction peaks at 13.1° and originated from the (100) plane because of the in-plane ordering of tri-s-triazine units, which is consistent with the literature [23]. As seen in Fig. S1B, the N₂ adsorption–desorption isotherms of the obtained mpg-C₃N₄ are type IV and have an apparent hysteresis loop that initiates at about 0.7 partial pressure, thereby indicating that the catalysts exhibit mesoporous structure. Table 1 presents the BET surface area (S_{BET}) of the mpg-C₃N₄ catalyst

Table 1
Structural properties of fresh mpg-C₃N₄ and reclaimed mpg-C₃N₄.

| Sample | S_{BET} (m ² /g) | D (nm) | V_{p} (cm ³ g ⁻¹) |
|---|--------------------------------------|--------|---|
| Fresh mpg-C ₃ N ₄ | 194 | 15.3 | 0.798 |
| Reclaimed mpg-C ₃ N ₄ | 161 | 14.7 | 0.594 |

(about 194 m²/g), which is consistent with that obtained in the literature [24]. As shown in Fig. S1C, the obtained mpg-C₃N₄ sample shows a sheet structure. All these characterizations showed that the mpg-C₃N₄ sample was successfully synthesized.

3.1. Catalytic performance of mpg-C₃N₄

ODS was performed under illumination and dark conditions to prove that the synthesized mpg-C₃N₄ can act as a photocatalyst for DBT oxidation with the oxygen molecule as the oxidant. As shown in Fig. 1I, the desulfurization rate increases with the reaction time and can achieve 100% at 90 min under illumination. However, when the reaction is performed in the dark, DBT removal is only 41%, which may be attributed to methanol extraction and mpg-C₃N₄ adsorption. These results demonstrated that illumination is essential for DBT removal in the ODS process. In order to explore the effect of specific surface on the photocatalytic activity, mpg-C₃N₄ and g-C₃N₄ were applied to the ODS process, respectively. As shown in Fig. 1II, the desulfurization rate of g-C₃N₄ is so far

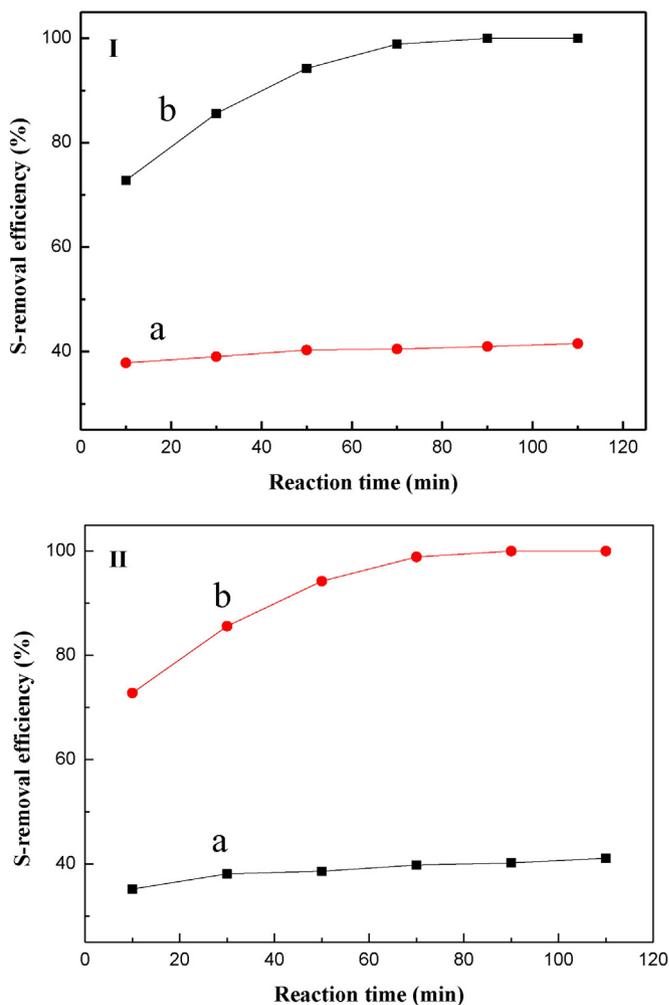


Fig. 1. I) Effect of a) darkness, b) visible light on S-removal efficiency; II) Effect of specific surface area on S-removal efficiency; (a) with C₃N₄; (b) with mpg-C₃N₄. Reaction condition: illumination time, 90 min; catalyst dosage, 0.1 g/10 ml.

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