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# Integrating $MoS_2$ on sulfur-doped porous g-$C_3N_4$ iostype heterojunction hybrids enhances visible-light photocatalytic performance

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## ABSTRACT

$MoS_2$/S-doped porous g-$C_3N_4$ ($MoS_2$/SPGCN) hybrids were fabricated via a facile calcination and ultrasound assembly method. Structural characterization indicated $MoS_2$ nanosheets were successfully loaded on SPGCN isotype heterojunction hybrids. The $MoS_2$/SPGCN photocatalysts showed more visible light absorption, larger specific surface area, and faster electron-hole separation. $MoS_2$/SPGCN significantly accelerated Rhodamine B photodegradation under visible light irradiation, which was mainly because the enriched active sites, broadened visible light absorption, and newly-formed heterojunction between $MoS_2$ nanosheets and SPGCN together suppressed the recombination of photoinduced electron-hole pairs. $MoS_2$/SPGCN also showed excellent recyclability and chemical stability. Thus, this work presents a good strategy of designing efficient photocatalysts by substituting the single catalyst base with metal-free isotype heterojunction hybrids.

## 1. Introduction

Challenges of fossil crisis and environmental pollution are pernicious to the human living ecosystem. One of the most promising and attractive solutions is photocatalytic technology, which can directly harvest and convert the renewable clean solar energy into sustainable energy and thereby degrade pollutants [1–3]. Numerous research efforts have been made to develop novel heterogeneous photocatalysts and construct the matched potential catalyst system [4–6]. Various efficient photocatalysts have been reported for hydrogen generation and contaminant photodegradation, but their applications are mostly limited by several challenges: (i) the rare and expensive raw materials for preparation of noble-metal semiconductors (e.g.$Ag_3PO_4$ [7], $Ag_3VO_4$ [8]); (ii) low stability of metal sulfide semiconductors (e.g. CdS [9], CuS [10]); (iii) low quantum efficiency of metal oxide photocatalysts (e.g.$TiO_2$ [11], ZnO [12]) in the visible light range. Thus, it is still challenging to develop appropriate visible-light-driven (VLD), cheap, photostable and nontoxic photocatalysts with a matched photocatalytic system.

Graphitic carbon nitride (g-$C_3N_4$), a fascinating metal-free conjugated polymer with superior photochemical stability, nontoxicity and low-cost, has been extensively studied in water pollutant decomposition, water splitting and $CO_2$ photocatalytic conversion under visible light irradiation since its discovery as a VLD photocatalyst [12–15]. Unfortunately, like most individual photocatalysts, the application of pure g-$C_3N_4$ is severely limited by low quantum efficiency due to poor charge separation and low visible light utilization [16,17]. Various effective modification strategies have been proposed, including mesoporous, porous or hollow nanostructure amelioration [18–21], doping with metal or nonmetal [22–24], and the widely-used g–$C_3N_4$–based semiconductor heterojunction [25–27]. However, most of these heterojunction hybrids are composed of pure g-$C_3N_4$. Zhang et al. prepared $C_3N_4$/sulfur-mediated $C_3N_4$ isotype heterojunction hybrids using trithiocyanuric acid and dicyandiamide and attributed the improved $H_2$ evolution photocatalytic performance to the prolonged lifetime of charge carriers due to the accelerated charge

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migration and separation [28]. Tan et al. fabricated mesoporous g-$C_3N_4$/g-$C_3N_4$ hybrids via template-calcination using melamine and amino cyanamide as co-precursors and $SiO_2$ as the template and improved the VLD methyl orange photodegradation activity by five times due to the larger specific surface area and the pore structure [29]. Therefore, photocatalytic activity can be improved by substituting pure g-$C_3N_4$ base with g-$C_3N_4$ isotype heterojunction hybrids.

G-$C_3N_4$ with different band gaps, morphologies and specific surface areas can be easily fabricated by thermal condensation of different precursors [30]. In particular, porous g-$C_3N_4$ with more active sites and larger specific surface area can be prepared by using urea as a precursor [31]. Thiourea is a precursor containing the sulfur group that acts as the leaving group to dissociate and regulate the thermal polycondensation, simultaneity, and sulfur-doping of g-$C_3N_4$ [32]. In all, S-doped porous g-$C_3N_4$ (SPGCN) isotype heterojunction hybrids fabricated by thermal condensation of urea and thiourea are worthy of expectation and research.

Two-dimensional $MoS_2$ with an intrinsic layered structure is extensively used as a synergistic co-catalyst of semiconductor materials to form heterojunctions, owing to its high visible light absorption ability, narrow band gap and photostability [33]. The heterojunction combination of g-$C_3N_4$ and $MoS_2$, because of nearly perfect band alignment, can easily promote the migration and separation of photoinduced carrier charge and significantly inhabit the recombination [34]. Many efforts have been made to fabricate $MoS_2$/g-$C_3N_4$ heterojunction photocatalysts, since $MoS_2$ as a synergistic co-catalyst effectively promotes the electron-hole separation and enhances photocatalytic activity [35–37]. Therefore, integrating $MoS_2$ on g-$C_3N_4$ isotype heterojunction hybrids through a facile and environment-friendly method accompanied by element doping and pore structure regulation is an attractive and significant trend.

In this study, $MoS_2$/SPGCN heterojunction composites were synthesized by a facile calcination and self-assembly method, characterized and evaluated in terms of Rhodamine B (RhB) degradation performance under visible light irradiation. The composites were significantly more photoactive due to the formation of heterojunction and the synergistic effect between $MoS_2$ and g-$C_3N_4$ isotype heterojunction hybrids. The possible mechanism was proposed after radical capturing experiments.

## 2. Experimental

### 2.1. Materials

Molybdenum disulfide ($MoS_2$), melamine ($C_2H_6O$), thiourea ($CH_4N_2S$), isopropanol (IPA, $C_3H_8O$), *p*-benzoquinone (p-BQ, $C_6H_4O_2$) and ethylenediaminetetraacetic acid ($Na_2$-EDTA, $C_{10}H_{18}N_2Na_2O_{10}$) (all Aladdin Industrial Corporation, Germany) were analytical reagents and used as-received. Distilled water was used throughout all processes. The reference pollutant was RhB from the textile industry.

### 2.2. Preparation of SPGCN isotype heterojunction hybrids

SPGCN hybrids were prepared via a facile calcination condensation method: 3 g of thiourea and 10 g of urea were heated at 8 °Cmin$^{-1}$ in a coved crucible under air atmosphere and 550 °C in a muffle furnace for 3 h. Bulk g-$C_3N_4$ (BGCN) was prepared from melamine via the same method. SGCN and PGCN were prepared from the precursors of thiourea and urea, respectively. Then the samples were ground into fine powder.

### 2.3. Preparation of $MoS_2$/SPGCN heterojunction nanocomposites

$MoS_2$/SPGCN composites were prepared via a facile ultrasonic method: 0.5 g of SPGCN powder and 0.025 g of $MoS_2$ were dissolved in 80 mL of ethanol and stirred at room temperature for 15 min. After 4 h of ultrasonication, the mixed slurry was stirred at 80 °C for complete ethanol evaporation, and then the precipitates were washed three times with pure water and ethanol. $MoS_2$/BGCN as a control was prepared similarly.

### 2.4. Characterization

Samples were characterized on a Bruker D8 Advance X-ray diffractometer (XRD, 40 kV, 40 mA, $2\theta = 10–80°$ at 8 °min$^{-1}$, Cu-K$\alpha$ radiation), a JEM-2100 transmission electron microscope (TEM, acceleration voltage = 200 kV), a Thermo ESCALAB250 X-ray photoelectron spectroscope (XPS, Al K$\alpha$ radiation), a Cary 500 ultraviolet–visible diffuse reflectance spectrometer (DRS), and an Edinburgh Shimadzu RF-5301 photoluminescence (PL) spectrophotometer (360 nm, room temperature). Nitrogen adsorption-desorption isotherms were recorded on a Micromeritics Tristar 3000 analyzer at 77.4 K.

### 2.5. Photocatalytic activity evaluation

Photocatalytic activity was evaluated by RhB degradation experiments (50 mL, 10 mg/L) in a photoreaction vessel under visible light irradiation (500 W Xe arc lamp with 420-nm cut-off filter). The solutions were stirred in the dark for 30 min, which ensured the adsorption-desorption balance between the photocatalyst and RhB. During the degradation reactions, the suspensions were stirred, sampled at an interval of 1 mL/5 min, diluted to 3 mL with deionized water and centrifuged at 10000 rpm for 5 min. Then RhB concentrations were measured at 554 nm on a UV-3600 UV–Vis spectrophotometer (Spectrumlab 752s, Xunda, Shanghai). In each radical-capture experiments, 50 mL of an RhB solution (10 mg/L) was added with 1 mmol $Na_2$-EDTA, 1 mmol IPA or 0.02 mmol BQ for measurement of RhB concentration change.

## 3. Results and discussion

### 3.1. Structural and morphological characterization

The crystal structures and phase compositions of BGCN, SGCN, PGCN and SPGCN were characterized by XRD (Fig. 1). The four g-$C_3N_4$ products all show two peaks at ~13.1 and 27.3° corresponding to the (100) and (002) planes of g-$C_3N_4$ (JCPDS no.87-1526), respectively, which are ascribed to in-plane packing motif of tris-triazine units and the inter-layer stacking of conjugated aromatic units, respectively [13,38]. The insert shows slight differences in the (002) plane among SGCN, PGCN and SPGCN, as the higher plane in SGCN versus PGCN (27.44 vs. 27.25°) was formed probably because the oxygen in the urea facilitated the condensation polymerization and reduced the inter-layer spacing [28,39]. The (002) plane of SPGCN (27.38°) lies in between SGCN and PGCN, which confirms the successful generation of isotype heterojunction [39,40]. The characteristic peaks of pure $MoS_2$ at 14.4°, 29.0°, 32.7°, 33.5°, 35.9°, 39.5°, 44.2°, 49.8°, 56.0°, 58.3° and 60.1° match well with the (002), (004), (100), (101) (102) (103), (006), (105), (106), (110) and (008) crystal planes of the orthorhombic form structure, respectively (JCPDS No.37-1492) [41,42]. $MoS_2$/SPGCN composites integrate the characteristics of $MoS_2$ and SPGCN and show a significantly weaker peak at 27.3° compared with SPGCN, indicating the conjugated aromatic system could be restrained due to the well combination and interaction [35,43]. $MoS_2$/BGCN composites showed the same