

# Synthesis of nitrogen-doped graphene–ZnS quantum dots composites with highly efficient visible light photodegradation



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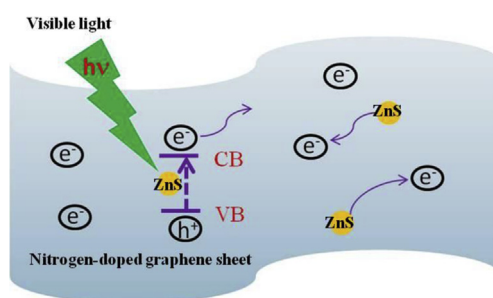
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## HIGHLIGHTS

- A new strategy was present to synthesize nitrogen-doped graphene–ZnS quantum dots (NG–ZnS QDs) composites.
- [(Zn<sub>2</sub>S<sub>2</sub>) (pa)] nanosheets were used not only as the sources of ZnS QDs but also as the sources of nitrogen.
- The photocatalytic activities of NG–ZnS QDs could be remarkably enhanced.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Nitrogen-doped graphene–ZnS quantum dots (NG–ZnS QDs) were synthesized by a one-pot hydrothermal process using graphene oxide and [(Zn<sub>2</sub>S<sub>2</sub>) (pa)] nanosheets as precursors. The results demonstrated that ZnS QDs deposited on the surface of the nitrogen-doped graphene (NG). Combined with series of our analysis and characterization, we found that [(Zn<sub>2</sub>S<sub>2</sub>) (pa)] nanosheets were used not only as the sources of ZnS QDs but also as the sources of nitrogen. Moreover, photocatalytic experiment of NG–ZnS QDs for organic dyes was conducted under visible light irradiation, and the results exhibited that the photocatalytic activities of resultant composites could be remarkably enhanced. This simple and catalyst-free approach for depositing ZnS QDs onto NG may provide an alternative way for preparation of other composites based on NG under mild conditions, which showed their potential applications in wastewater treatment.

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## 1. Introduction

Graphene sheets (GS), with unique physical and chemical properties associated with their two-dimensional (2D) single

monolayer form of sp<sup>2</sup> carbon atoms arranged in a honeycomb lattice, have attracted tremendous attention from theoretical and experimental scientists [1–5]. The deliberate introduction of dopants is an effective method to tailor the properties of GS. Theoretical calculations have suggested that doping with different heteroatoms can modulate the band structure of GS without impeding its good conducting behavior, some of which have been confirmed by experiments [6–10]. According to the previous literature, nitrogen doping is a way, which can both enhance the conductivity of GS,

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and induce n-type semiconductor behavior [10,11]. More importantly, incorporating different types of nitrogen into the carbon network would provide the nitrogen-doped graphene (NG) with more functional groups for property design [12,13]. Different techniques have been employed for the synthesis of NG. Li et al. have obtained doping levels of ~5% nitrogen through the exfoliation of graphite oxide in  $\text{NH}_3$  atmosphere at elevated temperatures [10]. Jafri et al. reported the synthesis of NG by using nitrogen plasma treatment of graphene and found that it shows improved performance of fuel cells with NG as catalyst supports [14]. Lai et al. have presented two different ways to fabricate NG and demonstrated its use as a metal-free catalyst for studying the catalytic active center for the oxygen reduction reaction (ORR) [15]. Panchakarla et al. have used the arc discharge for the synthesis of NG [11]. Wei et al. have prepared nitrogen-doped multilayer GS by adding  $\text{NH}_3$  gas during chemical vapor deposition growth of GS [9]. However, the arc discharge or nitrogen plasma usually requires rigorous conditions or special instruments. In case of chemical vapor deposition, the toxicity of nitrogen precursors ( $\text{NH}_3$  and pyridine) and possible contamination of the products by metal catalysts limit the practical applications of gas-phase synthesis. Therefore, it appears that it is still a challenge to explore simple and mild route to prepare NG.

In the past couple of decades, semiconductor nanostructures have been a subject of extensive interest due to their fundamental importance as well as enormous potential in optoelectronic, magnetic, and catalytic applications [16–18]. As one of typical II–IV binary semiconductor materials, zinc sulfide (ZnS) has received considerable concern due to its excellent properties. According to the previous reports, ZnS exists in two main crystalline forms: the cubic sphalerite phase and the hexagonal wurtzite phase. Both phases are direct and large band-gap semiconductors at room temperature (3.7 eV for the cubic sphalerite phase and 3.8 eV for the hexagonal wurtzite phase), regarded as good candidates for light-emitting materials, electroluminescent devices, photoluminescent devices, photocatalysts, solar cells, optical sensors, lasers, and optical recording materials [18–23]. ZnS nanomaterials with various nanostructures have been synthesized through different physical and chemical routes. For example, Huang et al. have designed and engineered a two-dimensional crystalline  $[(\text{Zn}_2\text{S}_2) (\text{pa})]$  nanostructure [24]. This compound is composed of double atomic layers of  $\text{Zn}_2\text{S}_2$  separated by organic n-propylamine. In order to improve the photochemical instability and photocatalytic activity of ZnS, researchers have focused on the synthesis of ZnS composites through combined ZnS with other semiconductors, such as  $\text{TiO}_2$ , CdSe, ZnO, CdS, and so on. Generally, to enhance photocatalytic activity of these semiconductor matrix systems, it is essential to retard the recombination of electron-hole species in the semiconductors by molecular electron relay semiconductor structures or efficient electron transport matrices, such as conductive polymer films or carbon nanotubes (CNTs) [25–28]. The delocalized conjugated materials are well matched with the photocatalysts in energy level and an intensive interface hybrid effect emerges between these materials, causing rapid charge separation and slow charge recombination in the electron-transfer process. The superior electrical conductivity and the springy atom-thin two-dimensional (2D) feature of graphene would make itself an excellent electron-transport matrix [1,29–31]. Nowadays, research about graphene-quantum dots (QDs) composites has become one of the hottest fields. However, to the best of our knowledge, little work has been done on nitrogen-doped graphene–ZnS quantum dots (NG–ZnS QDs) composites.

Herein, we present a new strategy to synthesize NG–ZnS QDs by use of deionized water as a solvent. In the synthesis procedure,  $[(\text{Zn}_2\text{S}_2) (\text{pa})]$  nanosheets were used not only as the sources of ZnS but also as the sources of nitrogen. This environmentally friendly

method for synthesis of NG–ZnS QDs composites can be successfully carried out in aqueous medium. Therefore, such an aqueous synthetic strategy may be potentially applicable to fabrication of other NG–semiconductor QDs composites. Moreover, the as-prepared NG–ZnS QDs hybrids have been used for removing organic dyes from water under visible light irradiation. Interestingly, it was found that the photocatalytic activities of the resultant composites could be remarkably enhanced. Therefore, such NG–ZnS QDs composites have potential applications in wastewater treatment.

## 2. Experimental section

All starting chemicals are of analytical grade and used without further purification, deionized water was used as solvent.

### 2.1. Synthesis of $[(\text{Zn}_2\text{S}_2) (\text{pa})]$ nanosheets

Hybrid  $[(\text{Zn}_2\text{S}_2) (\text{pa})]$  products were prepared according to literature. Briefly, the powder of  $[(\text{Zn}_2\text{S}_2) (\text{pa})]$  was prepared from solvothermal reaction of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (1.192 g, 4 mmol), S (0.064 g, 2 mmol) and n-propylamine (8 mL) in a 50 mL autoclave. After being cooled to room temperature naturally, the mixture was washed with deionized water and absolute alcohol several times followed by drying in anhydrous ethyl ether.

### 2.2. Preparation of the NG–ZnS QDs

In a typical procedure, 200 mg of graphite oxide (GO) (synthesized from graphite by Hummers' method) was dispersed in 20 mL distilled water by ultrasonication to get a homogeneous colloid, and then 200 mg of  $[(\text{Zn}_2\text{S}_2) (\text{pa})]$  nanosheets were dispersed into the above GO homogeneous solution by ultrasonication for 30 min. Then the mixture was transferred into a Teflon-lined stainless-steel autoclave with a volume of 50 mL. The autoclave was maintained at 180 °C for 12 h and finally cooled to room temperature naturally. The Teflon-lined stainless-steel autoclave can provide high pressure and temperature for the reaction. After being washed with deionized water and absolute alcohol several times, the gray black precipitates were obtained and dried in vacuum at 60 °C for 3 h.

### 2.3. Characterization

Several analytical techniques were used to characterize the synthesized products. The powder X-ray diffraction (XRD) patterns of the as-synthesized samples were recorded with a Japan MAPAHF X-ray diffractometer equipped with graphite-monochromatized  $\text{Cu K}\alpha$  irradiation ( $\lambda = 0.154056 \text{ nm}$ ), employing a scanning rate of  $0.02^\circ \text{ s}^{-1}$  in the  $2\theta$  range of 3–60°. Infrared (IR) spectrum analyses were operated on samples palletized with KBr powders in the range  $4000\text{--}400 \text{ cm}^{-1}$ , using an IR Fourier transform spectrophotometer (Nicolet, ZOSX). Selected area electron diffraction (SAED) patterns, high-resolution transmission electron microscopy (HRTEM) images, and transmission electron microscopy (TEM) images were obtained on a Hitachi model H-800 transmission electron microscope with an accelerating voltage of 200 Kv. X-ray photoelectron spectra (XPS) were taken on a Thermo ESCALAB 250 X-ray photoelectron spectrometer with Al  $\text{K}\alpha$  radiation. Thermogravimetric analyses (TGA) of samples were carried out with a Q5000 thermal analyzer (TA Co., USA) from 30 °C to 700 °C at a heating rate of  $10^\circ \text{ C min}^{-1}$  in air atmosphere (flow rate of  $100 \text{ ml min}^{-1}$ ). Ultraviolet–visible diffuse reflectance spectroscopy and ultraviolet–visible absorption spectra were recorded on a Perkin–Elmer Lambda 950 UV/Vis–NIR spectrophotometer (Perkin–Elmer). Photoluminescence spectra of the samples were

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