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# Kinetics and mechanism of enhanced photocatalytic activity employing ZnS nanospheres/graphene-like $C_3N_4$

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ABSTRACT

In this work, a novel photocatalyst ZnS nanospheres/graphene-like g-$C_3N_4$ (ZnS/GL-$C_3N_4$) nanocomposite was synthesized by a simple agitation method. Two-dimensional (2D) nanomaterial GL-$C_3N_4$, synthesized by thermal exfoliation from g-$C_3N_4$, showed large surface area and manifested efficient photocatalytic activity than bulk g-$C_3N_4$. ZnS nanospheres were well anchored and covered on the surface of GL-$C_3N_4$ nanosheets and a synergetic effect between the ZnS and GL-$C_3N_4$ could highly contributed to improvement of the light adsorption capability of GL-$C_3N_4$ as well as increasement of the separation efficiency of photon-generated $e^-$-$h^+$ pairs, therefore, enhancing its photocatalytic performance under the illumination of visible light. Methyl orange (MO, a kind of organic dyes which is hard to be degraded by pure $C_3N_4$) and tetracycline (TC, a representative broad-spectrum colorless antibiotic agent) were chosen as the targets of pollutants for degradation in this study. The optimum photocatalytic MO degradation of ZnS/GL-$C_3N_4$ (50%) was almost 3.48 and 12.4 times higher than that of pure ZnS and GL-$C_3N_4$, respectively. 91% TC was photodegraded in the presence of ZnS/GL-$C_3N_4$ (50%) and higher than that of GL-$C_3N_4$. Furthermore, kinetics and possible photocatalytic mechanism of MO degradation under visible light was proposed in detail. Except for the synergetic effect, the trapping experiments and ESR spectra demonstrated that not only $O_2^{\bullet-}$ and holes, but also $^{\bullet}OH$ were active species playing an importing role in this system for effective degradation. Our research results open an easy pathway for developing highly efficiency photocatalyst.



## 1. Introduction

Energy is the material basis of human survival and the important material guarantee of economic sustainable development [1]. However, with the development of society, energy and environmental issues are becoming grave threats to the sustainable development of human society [2]. Solar energy has attracted more and more attention, due to its inexhaustible, clean, renewable properties. Semiconductor-based photocatalysis via sunlight-driven photoredox reactions to mineralize organic pollutants or to directly convert solar energy into chemical energy is regarded as a long-term solution to completely eliminate the environmental issues and energy shortage [3].

As we all know, $TiO_2$ is widely used as semiconductor photocatalyst in environmental remediation for its high photocatalytic activity, non-toxicity, cheap and readily availability, chemical stability, and other advantages. However, the traditional $TiO_2$ has limitations on visible light application, due to its wide band gap [4]. It is urgent to seek for efficient visible light driven photocatalysts. Graphitic carbon nitride (g-$C_3N_4$) is one of non-metal semiconductor, possessing high thermal and chemical durability as well as the interesting electronic properties, which have made them become a kind of significant materials in the field of photocatalysis [5,6]. It has been reported that the band gap energy of g-$C_3N_4$ is 2.7 eV, making it be a good photocatalyst for use of visible light [7]. However, the photocatalytic efficiency of g-$C_3N_4$ is limited because of the high recombination rate of $e^-$-$h^+$ pairs [5]. On the other side, the special electronic structure of g-$C_3N_4$ make it be an excellent candidate for all sorts of functional materials to be coupled with, such as $TiO_2$/g-$C_3N_4$ [8], ZnO/g-$C_3N_4$ [9], $MoS_2$/g-$C_3N_4$ [10], rGO/g-$C_3N_4$ [11], AgX/g-$C_3N_4$ [7], which can decrease the high recombination rate of $e^-$-$h^+$ pairs and thus improve the photocatalytic performance [12,13].

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It is well known that ZnS has some advantages as a good photocatalyst with eco-friendliness, excellent stability, and low cost [14]. It can rapidly generate electrons and holes by photoexcitation and has higher negative reduction potentials of the excited electrons. However, the photocatalytic efficiency of ZnS is limited for its confined surface area, low transference ability of the photoexcited carriers [14], and the most important inherent defect-wide band gap (about 3.45 eV) which imposes restrictions on its photocatalytic application in the visible-light region [15]. As a result, coupling g-$C_3N_4$ with ZnS together to construct a g-$C_3N_4$/single metal sulfide photocatalyst [12] is a favorable way to enhance photocatalytic performance in the visible light region [16–19]. Unfortunately, the recombination rate of $e^-$-$h^+$ pairs of g-$C_3N_4$/ZnS nanocomposite is still high due to the own flaws of bulk g-$C_3N_4$. It has been reported that reduce the thickness of g-$C_3N_4$ [1], especially g-$C_3N_4$ monolayer structure has high electron and hole transfer property. Therefore, using the g-$C_3N_4$ monolayer or few layer structures to form the nanocomposite is a way to get the high photocatalytic activity. So we expect to achieve much thinner g-$C_3N_4$ and uniformly ZnS morphology, in order to synthesize the g-$C_3N_4$/ZnS nanocomposites with high photocatalytic activity. According to reports, few layer or graphene-like g-$C_3N_4$ (GL-$C_3N_4$) [20] synthesized by thermal exfoliation from g-$C_3N_4$, possessing 2D thin-layer structure with 6–9 atomic thickness (2–3 nm), large specific surface area, enhanced photocurrent response and electron transport ability, manifested efficient photocatalytic activity under visible light [21], and could be used as a photo-electrochemical sensor [1]. As we investigated, most of the photocatalysts took rhodamine B (RhB) as the target of pollutants which was easier to be degraded compared with methyl orange (MO) and yet the common colorless antibiotics degradation has not been studied. Tetracycline (TC), as a representative colorless broad-spectrum antibiotic agent, would cause multiple negative influences of the hierarchical system by inducing proliferation of bacterial drug resistance. Therefore, it is very important for the removal of TC and it was chosen as the degradation target to evaluate the photocatalytic activity of the photocatalyst. Meanwhile, the photocatalytic degradation mechanism has not been clearly clarified.

In this work, ZnS nanospheres/GL-$C_3N_4$ (ZnS/GL-$C_3N_4$) nanocomposites were synthesized by depositing ZnS nanospheres onto the GL-$C_3N_4$. We demonstrated that GL-$C_3N_4$ provided large surface area for the uniform distribution of ZnS nanospheres leading to the improved adsorption capability ZnS nanospheres with high surface also enhanced the contact areas in nanocomposits. The interaction between ZnS and GL-$C_3N_4$ allowing the effective charge transfer and promoting the photo-generated $e^-$-$h^+$ pairs separation, which would highly make contribution to the improvement of the pollutants degradation. MO and TC were chosen as the targets of pollutants in this system for one was hard to be degraded by $C_3N_4$ and another was a representative broad-spectrum colorless antibiotic agent, respectively. The photocatalytic efficiency of MO degradation over ZnS/GL-$C_3N_4$ was conducted under the illumination of visible light, which showed almost 3.48 and 12.4 times higher than that of pure ZnS and GL-$C_3N_4$, respectively. 91% TC was photodegraded in the presence of ZnS/GL-$C_3N_4$ (50%) higher than that of GL-$C_3N_4$. Photoluminescence (PL) spectra clearly showed that the introduction of ZnS decreased the recombination rate of photo-generated $e^-$-$h^+$ pairs, which improved the photocatalytic efficiency of GL-$C_3N_4$. GL-$C_3N_4$ has lager band gap energy (2.85 eV) and more negative CB level compared with g-$C_3N_4$. It was favorable for energy band alignment construction with ZnS nanospheres which can serve as the acceptor of the photo-generated electrons coming from GL-$C_3N_4$. It was also demonstrated that both $O_2^{\bullet -}$, $^{\bullet}OH$ and holes were the active species in photocatalytic degradation under the illumination of visible light. Moreover, a possible mechanism was also proposed in detail.

## 2. Experimental section

### 2.1. Preparation of photocatalysts

The materials were analytical grade (99%), and used as received without any purification. GL-$C_3N_4$ were synthesized according to the reported procedure [1]. ZnS nanosphere was synthesized by using a simple hydrothermal method: 1 mmol $ZnAc_2{\cdot}2H_2O$ and 1.5 g PVP were dispersed in 20 mL deionized water by mechanical stirring for 6 h, then TAA (1 mmol) was dropped into the mixture to active a clear solution. Then the clear solution was then transferred to a 20 mL Teflon-lined stainless steel autoclave and kept in an oven at 180 °C for 6 h. At last the product was collected by centrifugation, washed with distilled water and absolute ethanol repeatedly, and then dried to get the sediment.

The ZnS/GL-$C_3N_4$ nanocomposite photocatalysts were synthesized by mechanical agitation method. In a typical synthesis, 0.005 g ZnS and 0.095 g GL-$C_3N_4$ were dispersed in 50 mL distilled water by ultra-sonication for 60 min, and then the mixture was mechanical stirring for 48 h. At last, the product was collected by centrifugation, washed with deionized water and ethanol repeatedly, and then dried at 60 °C. The as prepared sample was named as ZnS/GL-$C_3N_4$ (5%). Several samples with different weight percent of ZnS (10 wt%, 20 wt%, 40 wt% and 50 wt%) were synthesized by using the similar procedure, and labeled as ZnS/GL-$C_3N_4$ (10%), ZnS/GL-$C_3N_4$ (20%), ZnS/GL-$C_3N_4$ (40%), ZnS/GL-$C_3N_4$ (50%), respectively.

### 2.2. Characterization of photocatalyst

The crystal structure of ZnS/GL-$C_3N_4$ nanocomposites were investigated by power X-ray diffraction (XRD) measurements which were performed on Bruker D8 diffractometer using Cu Kα radiation (λ = 1.5418 Å). The chemical state of elements was analyzed by X-ray photoelectron spectroscopy (XPS) on an ESCA Lab MKII X-ray photo-electron spectrometer using Mg Kα line source. The microstructure and grain morphology were researched by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM was taken with a FESEM MO del JEOL JSM-7001F and TEM was used a JEOL-JEM-2010 (JEOL, Japan) operated at 200 kV. The chemical composition was investigated by X-ray energy dispersion spectrum (EDS) performed at an acceleration voltage of 10 kV. UV–vis diffuse reflection spectra (DRS) were performed on UV-2450 UV–vis system (Shimadzu, Japan) with the reflectance standard material of $BaSO_4$. Photocurrents and electrochemical impedance spectroscopy (EIS) were recorded on CHI 660B electro-chemical workstation (Chenhua Instrument Company, China). PL experiments were conducted under a 325 nm light excitation . X-band Electron Spin Resonance (ESR) spectra were operated on a JES FA200 spectrometer at ambient temperature.

### 2.3. Photocatalytic degradation

Photocatalytic properties of photocatalysts were estimated by the degradation of MO and TC under the illumination of 300W Xe lamp with 400 nm cut-off filter in custom-made photochemical reactor at 30 °C under constant stirring. In every experiment, 0.0500 g photocatalyst powder was added in 50 mL of MO solution (10 mg $L^{-1}$) or TC (20 mg $L^{-1}$). The reaction mixture was continuously aerated by a pump to provide $O_2$. Prior to illumination, the mixed liquor was magnetically stirred in dark for 30 min to ensure an adsorption-desorption equilibrium between photocatalyst and pollutant. During every interval, 4.0 mL solution suspension would be taken out to separate the photocatalyst by