Sulfur-doped carbon nitride as a non-metal heterogeneous catalyst for sulfate radical-based advanced oxidation processes in the absence of light irradiation

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ABSTRACT

As graphene-like materials are demonstrated as non-metal catalysts to activate persulfate (PSF)/peroxymonosulfate (PMS), co-doping sulfur and nitrogen with graphene is a promising approach to improve catalytic activities. In this study, a convenient one-step approach is adopted to prepare sulfur-doped graphitic carbon nitride (SCN), which shows crumpled morphology and porosity on its surface, making SCN exhibit a much higher surface area than the common CN. Chemical analyses also confirm that a part of N atoms in CN skeleton are substituted by S. To evaluate PSF/PMS activation by SCN, decolorization of Rhodamine B (RhB) is selected as a model test. SCN showed a much higher catalytic activity than carbon nitride (CN) to activate PSF/PMS for RhB decolorization. Behaviors of PSF/PMS activation by SCN are explored by evaluating various effects on RhB decolorization, including temperature, pH, and salt. SCN-activated PSF/PMS for RhB decolorization is much favorable at elevated temperatures and neutral conditions. The presence of NaCl does not significantly inhibit the PSF/PMS activation by SCN. Several radical inhibitors on SCN-activated PMS are also evaluated and the RhB mechanism is shown to involve both sulfate and hydroxyl radicals. Potential mechanisms of PSF/PMS activation by SCN are proposed and ascribed to the more active carbon sites of SCN induced by the co-dopants of sulfur and nitrogen. SCN can be also re-used to activate PSF/PMS without catalytic activity loss. These features demonstrate that SCN is a conveniently-prepared but effective and sustainable non-metal heterogeneous catalyst for activating PSF/PMS.

1. Introduction

Wet chemical oxidation (WCO) is an extensively employed reaction for chemical synthesis [1] as well as environmental remediation [2]. In particular, processes of WCO for treating organic contaminants are categorized as Advanced Oxidation Processes (AOPs) [2]. AOPs generally involve two high-oxidation-potential radicals: hydroxyl (OH·) and sulfate radicals (SO$_4$·$^-$) [3]. While OH·-involved AOPs have been intensively used, SO$_4$·$^-$-involved AOPs are also increasingly developed owing to several advantageous features of SO$_4$·$^-$, including comparable/higher oxidation power, higher selectivity towards aromatic contaminants and longer half-life [4].

Generally, sulfate radicals are derived from strong oxidants, such as persulfate (PSF) and peroxymonosulfate (PMS), which are commercially available and environmentally friendly [4]. Therefore PSF and PMS have been employed in many applications, such as organic synthesis [5], disinfection [6], and environmental pollution control [4]. Nevertheless, the generation of SO$_4$·$^-$ from self-decomposition of PSF/

PMS is quite slow; therefore catalysts are required to "activate" PSF/PMS. Several transition metals (*e.g.*, cobalt, copper, iron and manganese) have been proposed to activate PSF/PMS; however usage of homogeneous or heterogeneous transition metallic catalysts inevitably leads to secondary pollutions and relatively high costs/environmental impacts.

Thus, recently a number of non-metal heterogeneous catalysts are proposed, including carbonaceous [7], graphene-based materials [8], graphitic carbon nitride (CN) [9], boron [10] and α-sulfur [11]. In general, activation of PMS/PSF by non-metal catalysts is considered to involve two types of mechanisms. In the first type of mechanism, PMS/PSF is "activated" by highly active species (*e.g.*, oxygenic groups of carbonaceous materials, nitrogen/sulfur groups doped in carbonaceous materials and defective sites) by receiving electrons [7,10,12–14]. The second type of mechanism of PMS/PSF activation is associated with the introduction of photo-generated active species derived from photocatalytic non-metal photocatalysts (*e.g.*, α- sulfur and carbon nitride) under light irradiation [11,14–16].

Since the light irradiation may involve additional energy input and relatively complicated protocols, it would be more attractive and practical to create efficient non-metal catalysts for activating PSF/PMS even without visible or UV light irradiation. As doping non-metal elements (*e.g.*, B, P, N or S) with graphene-like materials (*i.e.*, graphene and CN) is considered as a useful technique to enhance their reactivity [12], Duan et al. demonstrated that co-doping of sulfur and nitrogen with graphene significantly improved catalytic activity of graphene for activating PMS to degrade organic pollutants [8]. Even though these heteroatom-doped graphene-like materials are promising, preparation of these materials is relatively complicated and involving multiple steps and reagents [8]. To reduce preparation time and associated costs as well as environmental impacts, it is necessary to develop easy-to-prepare heteroatom-doped graphene-like materials. Herein, a commercial available compound consisting of carbon, nitrogen and sulfur, trithiocyanuric acid, is selected and used as a precursor for preparing such a sulfur-nitrogen co-doped graphene-like material. Through one-step heat treatment, trithiocyanuric acid can be conveniently converted to sulfur-doped graphitic carbon nitride (SCN) [17,18].

The resulting SCN is expected to exhibit relatively high reactivity and becomes a non-metal heterogeneous catalyst to react with PMS as well as PSF for generation of sulfur radicals even in the absence of light irradiation. To investigate catalytic activity of SCN for activating PSF/PMS, decolorization of a toxic dye, Rhodamine B (RhB), is selected as a model test to evaluate sulfate radicals derived from PSF/PMS activated by SCN. The reason for selecting RhB as a representative contaminant in this study is because RhB is potentially carcinogenic and frequently used in degradation studies using sulfate-radial based processes [15,19–21].

Behaviors of PSF/PMS activation by SCN are explored through examining various effects on RhB decolorization, including temperature, pH and co-existing ions. Effects of radical inhibitors are also examined to reveal the decolorization mechanism by SCN-activated PSF/PMS. A potential mechanism for SCN to activate PSF/PMS is also proposed based on the chemical configuration of SCN. Reusability of SCN for activating PSF/PMS is evaluated by re-using SCN multiple times without regeneration treatments.

2. Experimental

2.1. Synthesis and characterization of SCN

SCN was prepared according to reported protocols [17,18]. In brief, trithiocyanuric acid (Alfa Aesar, USA) was placed in a ceramic crucible and heated at 550 °C in N_2 atmosphere for 4 h to obtain SCN powders. To compare with SCN, undoped CN was also prepared by the same procedure using melamine powder (Sigma-Aldrich, USA) as a precursor. SCN was first characterized by a field emission SEM (JEOL JSM-6700, Japan) and a TEM (JEOL JEM-2010, Japan) to visualize its morphology. The XRD pattern of SCN was measured using an X-ray diffractometer (PANalytical, the Netherlands). Chemical characteristics of SCN were determined by X-ray photoelectron spectroscopy (XPS) (PHI 5000, ULVAC-PHI, Inc., Japan). N_2 sorption and desorption isotherms of SCN were obtained using a volumetric gas adsorption analyzer (Quantachrome Auto IQ, USA). Zeta potential of SCN was also measured by a zetasizer (Nano-ZS, Malvern Instruments Ltd, Malvern, UK).

2.2. PSF/PMS activation by SCN for decolorization of Rhodamine B (RhB)

To evaluate catalytic activity of SCN for activating PSF/PMS, batch-type decolorization of a toxic dye, Rhodamine B (RhB), was selected as a model reaction. In a typical experiment, PSF/PMS powder (300 mg L^{-1}) (Sigma-Aldrich, USA) was added to 0.2 L of RhB aqueous solution with an initial concentration (C_O) of 10 mg L^{-1}. Upon the dissolution of PSF/PMS powder, SCN powder (500 mg L^{-1}) was then added to the RhB solution. The mixture was stirred and its temperature was maintained at a fixed temperature. As SCN is a semiconductor [22], decolorization experiments were performed inside a customized dark room to prevent photocatalytic reactions induced by SCN. At pre-set intervals, sample aliquots were taken from the batch reactor and the residual RhB concentration (C_t, mg L^{-1}) was measured using a UV–vis spectrophotometer. Effects of radical inhibitors were also investigated to reveal the RhB decolorization mechanism by SCN-activated PSF/PMS. The inhibitors included methanol (0.2 M) and *tert*-butyl alcohol (TBA) (0.2 M).

The reusability of SCN was evaluated by continuously using SCN for activating PSF/PMS without regenerating SCN. Through examining the reusability of SCN, the stability and catalytic activity of SCN over long-term operation can be determined. In the typical experiment of reusability, the used SCN sample is recovered from solutions *via* centrifugation and then added to a subsequent batch-experiment without washing/treating the used SCN by any means.

3. Results and discussion

3.1. Characterization of SCN

Fig. 1(a) reveals that SCN sheets are crumpled as other studies reported [18,23]; however, the thin layer of SCN sheets can be still observed on the edge of crumpled SCN. A TEM image of SCN (Fig. 1(b)) shows that the crumpled SCN appear to be hollow with roughened surfaces and pores. Fig. 1(c) displays the crystalline structure of SCN, in which two prominent peaks can be detected at 13.3° and 27.2°, corresponding to (100) of the in-plane packing and (002) of the lamellar stacking of SCN [22], respectively. The textural properties of SCN are also determined using N_2 sorption isotherms (Fig. 1(d)) which seem to be the IUPAC Type III isotherm with a noticeable hysteresis loop. This suggests that crumpled SCN might exhibit mesopores, which can be validated by the pore size distribution shown in the inset in Fig. 1(d), confirming the porous texture of SCN. This crumpled and porous structure of SCN enables SCN to exhibit a much higher surface area as 86.8 $m^2 g^{-1}$ than typical CN (*ca.* 10 $m^2 g^{-1}$ [23]).

Surface chemistry of SCN was also determined by XPS as displayed in Fig. 2. A full-survey spectrum of SCN (Fig. 2(a)) reveals that SCN comprised carbon, nitrogen as well as sulfur. In particular, the core-level spectrum of C 1s (Fig. 2(b)) can be deconvoluted to display two peaks at 285.0 and 288.0 eV, attributed to C—C bond and the sp^2-bonded carbon of N—C=N, respectively. The core-level spectrum of N 1s (Fig. 2(c)) can be also deconvoluted to show two peaks at 398.5 and 399.8 eV, corresponding to the sp^2-hybridized aromatic N bonded to carbon (*i.e.*, C=N—C) and the tertiary N bonded to carbon (*i.e.*, N—(C)$_3$ or H—N—(C)$_2$), respectively [24]. On the other hand, the core-level spectrum of S 2p (Fig. 2(d)) can be deconvoluted to exhibit two peaks at 163.9 and 164.6 eV. The peak at 163.9 eV is attributed to C—S bond in which S substituted N atoms in CN skeleton [25]. The peak at 164.6 eV can be ascribed to the sulfur species in the bond of C—S—C [25]. These peaks validate that CN was doped with sulfur to form SCN. Surface property of SCN was further revealed by measuring the zeta potential of SCN. Fig. S1 (see **ESI**) shows that the surface of SCN became negatively-charged starting from pH = 4 and continued to decrease at higher pH values, indicating that SCN is highly negatively-charged.

To compare SCN with the undoped CN, CN was also prepared and its XRD pattern (Fig. S2(a)) is consistent with reported patterns (JCPDS card #87-1526). The XPS analysis of CN (Fig. S2(b)) also confirms the formation of CN [24].

3.2. Decolorization of RhB by SCN-activated PSF/PMS and its mechanism

Prior to evaluating SCN for activating PSF/PMS, it is necessary to determine whether SCN can decolorize RhB *via* adsorption. Fig. 3(a) shows that RhB was not decolorized in the presence of SCN, suggesting