



Metal-free activation of Oxone using one-step prepared sulfur-doped carbon nitride under visible light irradiation



Kun-Yi Andrew Lin*, Zhi-Yu Zhang

Department of Environmental Engineering, National Chung Hsing University, 250 Kuo-Kuang Road, Taichung, Taiwan

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ABSTRACT

While Oxone can be activated by catalysts for efficient generation of sulfate radicals, most of catalysts are transition metals, which could lead to secondary pollution and relatively high costs. Thus, non-metal catalysts consisting of earth-abundant elements are promising metal-free alternatives for activating Oxone. As graphitic carbon nitride (CN) has been demonstrated to activate Oxone under visible light irradiation, sulfur-doping CN (SCN) is expected to exhibit a relatively high catalytic activity for activating Oxone. However, few studies have been conducted to investigate SCN for activating Oxone. Additionally, SCN should be prepared conveniently to reduce usage of associated reagents during the doping. To this end, a one-step preparation method is adopted in this study to convert trithiocyanuric acid to SCN. The as-prepared SCN shows the morphology of crumpled micro-bags with porous surfaces, enabling it to exhibit a much higher surface area ($86.8 \text{ m}^2 \text{ g}^{-1}$) than typical CN (ca. $10 \text{ m}^2 \text{ g}^{-1}$). As Rhodamine B (RB) decolorization was employed as a model test to evaluate sulfate radicals generated from activation of Oxone, SCN also exhibited a much higher catalytic activity (rate constant (k_1) = 0.107 min^{-1}) to activate Oxone than CN ($k_1 = 0.037 \text{ min}^{-1}$). SCN-activated Oxone for RB decolorization was relatively favorable at elevated temperatures as well as neutral conditions; it also remained quite effective even in the presence of NaCl. Through examining effects of radical scavengers, the RB mechanism can be primarily attributed to sulfate radicals. SCN was also reusable to activate Oxone for RB decolorization over 6 cycles. These features indicate that SCN is an easy-to-prepare and promisingly effective non-metal catalyst to activate Oxone.

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1. Introduction

Advanced oxidation processes (AOPs) represent one of the most commonly adopted techniques to treat organic contaminants in wastewater [1–4]. In AOPs, high oxidation power radicals (e.g., hydroxyl and sulfate radicals) are generated and used to degrade organic molecules. Hydroxyl-radical generating processes have been intensively studied and developed, such as Fenton's reaction and photolysis. Sulfate-radical generating processes recently also gain much attention because sulfate radicals possess similar or even higher oxidation potentials than hydroxyl radicals. Sulfate radicals have been also proven to exhibit a much higher selectivity towards unsaturated and aromatic molecules with a significantly longer half-life (i.e., 30–40 μs) [5–8].

To generate sulfate radicals, Oxone (i.e., peroxymonosulfate (PMS) salt) has been an extensively used reagent because Oxone is environmentally benign and commercially available [9]. How-

ever, self-decomposition of Oxone for generating sulfate radicals is extremely slow and therefore catalysts are needed to facilitate the decomposition of Oxone, so-called "activation of Oxone". To date, many catalysts have been proposed to activate Oxone; however most of these catalysts are transition metals including iron, manganese, cobalt, and copper [10–16]. Usage of these transition metallic catalysts, regardless of whether they are homogeneous or heterogeneous catalysts, may cause secondary pollutions and require relatively high costs. Thus, a number of non-metal materials which consist of earth-abundant elements have been proposed as metal-free catalysts for activating Oxone, including reduced graphene oxide [17], graphene [18], graphitic carbon nitride (CN) [12,19], and α -sulfur [14]. Among these materials, CN and α -sulfur are particularly interesting as they are photocatalysts and therefore light irradiation can enable these materials to activate Oxone for degrading organic compounds [12,14,19]. Moreover, as CN is a semiconductor, doping CN with other non-metal elements (e.g., sulfur) is considered as a promising approach to improve its photocatalytic activity [20,21]. Nevertheless, few relevant studies have been conducted to investigate Oxone activation by

* Corresponding author.

E-mail address: linky@nchu.edu.tw (K.-Y.A. Lin).

sulfur-doped CN. On the other hand, conventional doping processes on graphene-like materials are relatively complex [22–24]. For example, preparation of nitrogen and sulfur co-doped graphene-analogue materials involves multiple steps. Firstly, graphene (or 2-D carbonaceous materials) must be obtained using the quite intensive chemical oxidation method (*i.e.*, Hummers' method), which could take up to a few days for exfoliating, washing and drying graphene-based materials. Then, a nitrogen precursor (*e.g.*, ammonium nitrate) and a sulfur precursor (*e.g.*, diphenyl disulfide) are mixed with the as-prepared graphene materials in water. The resulting mixture must be dried again to remove water, and then transferred to a muffle furnace for annealing at a high temperature. The annealed product has to be washed with water and alcohols repeatedly and dried to yield the final product, the sulfur-nitrogen co-doped 2D carbonaceous material. Thus, the traditional preparation for sulfur-nitrogen co-doped graphene analogues requires many reagents and steps, limiting development of sulfur-doped graphene-like materials for practical applications. In view of these issues, in this study, a one-step conversion method is adopted to use a commercially available and inexpensive compound trithiocyanuric acid, consisting of carbon, nitrogen and sulfur, as a precursor. Through the one-step heat treatment, trithiocyanuric acid is transformed to sulfur-doped CN without using any additional reagents and wet chemical preparation steps.

The as-prepared SCN was characterized using scanning and transmission electronic microscopies (SEM and TEM) for its morphology. Chemical characteristics of SCN were analyzed using X-photoelectron spectroscopy. Surface and textural properties of SCN were also measured to obtain its surface charges and N_2 sorption isotherms. To evaluate catalytic activity of SCN to activate Oxone for generation of sulfate radicals, decolorization a toxic dye, Rhodamine B (RB), was employed as a model reaction as dye-containing wastewater treatment has been intensively investigated using many approaches, including adsorption [25–28], chemical oxidation [29] and biological degradation [30]. Behaviors of Oxone activation by SCN under light irradiation were investigated by evaluating different effects on RB decolorization, including SCN and Oxone concentrations, temperature, pH and co-existing ions. Effects of radical scavengers were also examined to probe into the decolorization mechanism by Oxone activated by SCN. Recyclability of SCN for activating Oxone under light irradiation was also tested by re-using SCN for activating Oxone over multiple times without regeneration treatments.

2. Experimental

2.1. Preparation and characterization of SCN

Chemicals involved in this study are commercially available and used without purification. To prepare sulfur-doped graphitic carbon nitride (SCN), trithiocyanuric acid (Alfa Aesar, USA) was used as a precursor which was placed inside a ceramic crucible and heated at 550 °C in N_2 atmosphere to obtain SCN powders [31,32]. The undoped CN was also prepared by the above-mentioned heat treatment using melamine (Sigma-Aldrich, USA) as a precursor for comparing with SCN. The as-prepared SCN was characterized using a field emission SEM (JEOL JSM-6700, Japan) and a TEM (JEOL JEM-2010, Japan) for its morphology. Crystalline structures of SCN and CN were obtained by an X-ray diffractometer (PANalytical, the Netherlands). Surface chemistry of SCN was analyzed by X-ray photoelectron spectroscopy (XPS) (PHI 5000, ULVAC-PHI, Inc., Japan). The textural properties of SCN were measured by a volumetric gas adsorption analyzer (Quantachrome Auto IQ, USA). The surface charge of SCN was also determined

using a zetasizer (Nano-ZS, Malvern Instruments Ltd., Malvern, UK).

2.2. Activation of Oxone by SCN for decolorization of Rhodamine B (RB)

The catalytic activity of SCN for activating Oxone was evaluated by batch-type decolorization of RB. A typical decolorization experiment started from adding 300 $mg L^{-1}$ of Oxone powder to 200 mL of RB solution with a starting concentration (C_i , $mg L^{-1}$) of 10 $mg L^{-1}$. Once Oxone powder was dissolved, SCN was immediately added to the RB solution under visible light irradiation (150 W with a UV cut-off filter, Philips, Netherland). The resulting mixture was then stirred and its temperature was kept at a desired temperature. Sample aliquots were withdrawn from the RB solution and the residual RB concentration (C_t , $mg L^{-1}$) of each sample aliquot was determined by a UV-vis spectrophotometer. Effects of radical scavengers (0.2 M) (*tert*-butyl alcohol (TBA) and methanol) on RB decolorization were also examined to provide insights into RB decolorization mechanism by SCN-activated Oxone. To evaluate the recyclability of SCN for activating Oxone under visible light, SCN was re-used for activating Oxone over 6 cycles without any regeneration treatments.

3. Results and discussion

3.1. Characterization of SCN

Fig. 1(a) shows that the morphology of SCN appears like crumpled micro-bags and very thin layers of SCN sheets can be observed from breakages of these "micro-bags". A TEM image of SCN (Fig. 1(b)) further validates that these micro-bags of SCN are hollow with roughened surfaces. To determine its textural properties, N_2 sorption/desorption isotherms of SCN were measured in Fig. 2(a). The sorption isotherm can be classified as the IUPAC Type III isotherm with a noticeable hysteresis loop, suggesting that SCN might exhibit mesopores. The inset in Fig. 2(a) displays the pore size distribution of SCN with a range from 2 to 160 nm, confirming the existence of mesopores in SCN. The crumpled, hollow and porous morphology of SCN enables SCN to exhibit a significantly higher surface area as 86.8 $m^2 g^{-1}$ than typical CN (ca. 10 $m^2 g^{-1}$ [33]). It has been reported that the relatively high surface of SCN could be attributed to the decomposition of some trithiocyanuric acid during the heat treatment [31]. Therefore, more active sites should be obtained in SCN to facilitate catalytic/photocatalytic activities. The crystalline structure of SCN was determined and shown in Fig. 2(b); two noticeable peaks can be found at 13.3° and 27.2°, attributed to (0 0 2) of the lamellar stacking and (1 0 0) of the in-plane packing of SCN [20], respectively.

To analyze the surface chemistry of SCN, XPS analysis was adopted and a full-survey spectrum is shown in Fig. 3(a), indicating that SCN consisted of carbon, nitrogen, and sulfur. Core-level spectra of these elements are deconvoluted to further display chemical species of these elements. Fig. 3(b) shows the core-level spectrum of C1s which exhibits two peaks at 285.0 and 288.0 eV, corresponding to C—C bond and the sp^2 -bonded carbon of N—C=N, respectively. Fig. 3(c) reveals the core-level spectrum of N1s, and two peaks can be detected 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), respectively [34]. The core-level spectrum of S2p can be seen in Fig. 3(d), in which there are two peaks located at 163.9 and 164.6 eV, derived from C—S bond in which S substituted N atoms in CN skeleton [35] and the sulfur species in the bond of C—S—C [20,35], respectively.

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