



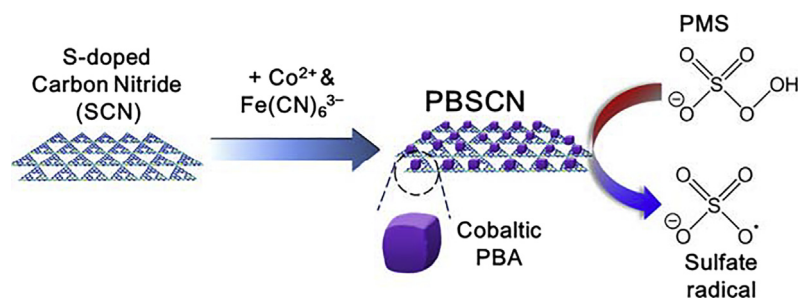
# Prussian Blue analogue supported on sulfur-doped carbon nitride as an enhanced heterogeneous catalyst for activating peroxymonosulfate

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## GRAPHICAL ABSTRACT



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## ABSTRACT

While Prussian Blue (PB) analogues are attractive catalysts for activating peroxymonosulfate (PMS), PB analogues are very small and thus difficult for recovery. Immobilizing PB particles onto graphene is a useful technique which facilitates recovery and also enhances catalytic activities. As doping graphene with sulfur/nitrogen (S/N) increases its electro-conductivity and active sites, the composite of PB and S/N-doped graphene should enhance PMS activation. Thus, this study aims to fabricate such a composite. Unlike conventional S/N-doped graphene prepared via post-modifications, trithiocyanuric acid is used as a precursor, which is converted to S-doped graphitic carbon nitride (SCN). The composite of PB and SCN (PBSCN) is then fabricated by growing a cobalt-based PB analogue on SCN. The resulting PBSCN preserves the crystalline structures, textural properties and catalytic sites of PB and SCN. As degradation of Acid Red 27 (AR) is used as a model reaction, PBSCN exhibits a higher catalytic activity than PB and SCN individually, as well as Co<sub>3</sub>O<sub>4</sub> to activate PMS for AR degradation possibly because SCN may facilitate electron transfer and enhance catalytic activities of PB. PBSCN also remains effective and re-usable over several cycles for AR degradation. These features indicate that PBSCN is a promising catalyst for activating PMS and the fabrication technique demonstrated here can be employed to prepare composites of various PB analogues and carbon nitride to exhibit enhanced catalytic activities.

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## 1. Introduction

Sulfate-radical (SO<sub>4</sub><sup>-•</sup>)-based advanced oxidation processes (AOPs) represent one of the most important approaches for treat-

ing organic contaminants as SO<sub>4</sub><sup>-•</sup> exhibits high oxidation potentials (2.5–3.1 V vs NHE), and preferably react with unsaturated and aromatic electrons. To obtain SO<sub>4</sub><sup>-•</sup>, potassium peroxymonosulfate (PMS) (KHSO<sub>5</sub>) has been intensively employed as a useful source because PMS is inexpensive, and environmentally-friendly [1]. Nevertheless, SO<sub>4</sub><sup>-•</sup> generation from the self-decomposition of

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PMS is incredibly slow and thus it requires “activation” in order to generate  $\text{SO}_4^-$  rapidly.

Even though many techniques have been proposed for activating PMS, the addition of catalysts is regarded as the most practical means for activating PMS [2–6]. While homogeneous metallic catalysts are firstly developed for activating PMS, the homogeneous nature of these catalysts make them difficult to recover, thereby leading to secondary pollution. Thus, many efforts have been made to develop heterogeneous metallic catalysts for activating PMS and particularly catalysts with hierarchical structures, high surface areas and porosities, and accessible metallic sites are considered as the most suitable catalysts for PMS activation [1,7].

In view of these desired features, a relatively new class of materials, Metal Organic Frameworks (MOFs), has received great attention because MOFs, comprised of metal sites as nodes and organic ligands as bridges, can exhibit hierarchical structures, enabling MOFs to possess high surface areas, ordered pores, and accessible metal sites. Thus, a few MOFs have been evaluated and validated to activate PMS [8]. Besides the typical MOFs, Prussian Blue (PB) analogues, formulated as a cubic  $\text{M}^{\text{II}}[\text{M}^{\text{III}}(\text{CN})_6]_2$  framework, are also considered as a special family of MOFs [9,10]. However, PB analogues are even more intriguing because different oxidation states of metal ions can exist within PB analogues [11]. In addition, frameworks of PB can comprise vacancies for balancing charges [11]. Thus, PB analogues have been intensively studied for catalytic applications [12–15].

While PB analogues seem as promising catalysts for PMS activation, PB particles are typically very small (a few tens of nanometers) [16,17], making it relatively hard for recovery. As immobilizing fine particles onto large-size substrates represents a useful approach, several studies have also attempted to immobilize metal-containing small particles on various supports for PMS activation [18–20]. Some of them even found that the immobilization on certain types of supports (e.g., carbonaceous materials) led to synergic effects, enhancing PMS activation [18–23]. Meanwhile, a few studies have also demonstrated that immobilization of PB analogues on substrates (i.e., carbonaceous materials, and metal oxides) can exhibit enhanced catalytic activities for electrocatalysis [24], photo-catalysis [25] and oxidative catalysis [26]. Thus, immobilization of PB particles on carbonaceous substrates may not only favor recovery but also enhance catalytic activities of PB for PMS activation. However, to our knowledge, very few studies relevant to this topic are available in literatures. Therefore, this study proposes to investigate the catalytic activities of PB immobilized on carbonaceous materials.

Although various forms of carbonaceous materials are available, sheet-like (2-dimensional) carbonaceous materials are highly attractive because they can provide large planar surfaces for supporting metallic particles. To this end, graphene sheets have been proven as an advantageous sheet-like carbon support, which also provides synergic effects to enhance PMS activation owing to its high electro-conductivity and electron-rich surfaces [20–22,27–29]. In addition, many studies report that heteroatom-doped (e.g., N and S) graphene can be even more catalytically active for PMS activation [30,31]. However, the fabrication of graphene-based materials through the conventional methods in fact is very time-consuming and complex [32,33]; doping graphene with N and S via post-modifications also requires multiple steps and long preparation time [33]. Therefore, it is necessary to employ a simple and convenient method for preparing sheet-like carbonaceous material doped with N and S as a support for PB.

In this regard, a special reagent, trithiocyanuric acid, is adopted in this study as a precursor, which is converted into S-doped graphitic carbon nitride (SCN) via a convenient one-step carbonization. The resulting SCN can be a sheet-like S/N-doped carbon support for immobilizing PB. As cobalt has been considered as

the most effective transition metal for PMS activation, a cobalt-based PB,  $\text{Co}_3[\text{Fe}(\text{CN})_6]_2$ , is specifically selected as a representative PB. The composite of PB and SCN (PBSCN) is fabricated conveniently by in-situ growing PB on SCN.

Catalytic activity of PBSCN for PMS activation is determined by batch-type experiments of degradation of a toxic azo dye, Acid Red 27 (AR). AR is a commonly-used dye, but it is carcinogenic [34,35]. Catalytic behaviors of PBSCN are studied by evaluating AR degradation by PBSCN-activated PMS under various conditions and the mechanism of AR degradation is determined by evaluating effects of radical scavengers and Electron Paramagnetic Resonance (EPR) analysis. Reusability of PBSCN for PMS activation is also studied without regeneration.

## 2. Experimental

### 2.1. Materials

All chemicals employed in this study were used as received without purification: cobalt nitrate ( $\text{Co}(\text{NO}_3)_2$ ) (reagent grade, 98%, Sigma-Aldrich, USA), potassium peroxymonosulfate (PMS) ( $\geq 47\%$   $\text{KHSO}_5$  basis, Sigma-Aldrich, USA), and Acid Red 27 (AR) (dye content 90%, Sigma-Aldrich, USA), potassium hexacyanoferrate ( $\text{K}_3\text{Fe}(\text{CN})_6$ ) (ACS reagent grade,  $\geq 99\%$ , J. T. Baker, Germany), trithiocyanuric acid ( $\geq 95\%$ , Alfa Aesar, USA), *tert*-butyl alcohol (TBA) (ACS reagent grade,  $\geq 99\%$ , Alfa Aesar, USA),  $\text{Co}_3\text{O}_4$  NP (< 50 nm) (99.5% trace metals basis, Sigma-Aldrich, USA). Deionized (DI) water was prepared to less than 18  $\text{M}\Omega\text{-cm}$ .

### 2.2. Preparation and characterization of PBSCN

The preparation of PBSCN can be schematically illustrated as shown in Fig. 1(a). SCN sheets were first prepared by carbonizing trithiocyanuric acid at 550 °C in  $\text{N}_2$  for 4 h. After washing and drying the as-prepared SCN, 1.0 g of SCN was dispersed in 100 mL of DI water under sonication for 30 min. Subsequently, 1.5 g of  $\text{Co}(\text{NO}_3)_2$  and 1.1 g of  $\text{K}_3\text{Fe}(\text{CN})_6$  were simultaneously added to the aforementioned SCN suspension. These amounts of reagents were employed particularly in order to obtain PBSCN with equivalent PB and SCN in terms of weights. The mixture was gently stirred at ambient temperature for 12 h, and the resulting precipitate was collected by centrifugation, washed repeatedly with ethanol and DI water, and dried at 80 °C to yield PBSCN composite.

PBSCN was characterized by a field emission SEM (JEOL JSM-6700, Japan) and a TEM (JEOL JEM-2010, Japan) for determining its morphology. Energy-dispersive X-ray spectroscopy (EDS) mapping analysis of PBSCN was conducted using an EDS accessory equipped to the SEM (Oxford Instruments, UK). The XRD pattern of PBSCN was obtained using an X-ray diffractometer (Bruker, USA). Surface chemistry of PBSCN was measured by X-ray photoelectron spectroscopy (XPS) (PHI 5000, ULVAC-PHI, Japan).  $\text{N}_2$  sorption and desorption isotherms of PBSCN and its precursors were measured by a volumetric gas adsorption analyzer (Quantachrome Auto IQ, USA). Thermogravimetric analyses of PBSCN and its precursors were investigated by a thermogravimetric analyzer (ISI TGA i1000, USA) in air.

### 2.3. Activation of PMS by PBSCN for AR degradation

PMS activation by PBSCN was evaluated using batch-type experiments of AR degradation. Typically, 20 mg of PMS was first added to 200 mL of AR solution with an initial concentration ( $C_0$ ) of 50 mg/L. When PMS powder was fully dissolved in the AR solution, 20 mg of PBSCN was added to the AR solution immediately. After pre-set intervals, sample aliquots were withdrawn for

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