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Nanostructured Co_3O_4 grown on nickel foam: An efficient and readily recyclable 3D catalyst for heterogeneous peroxymonosulfate activation

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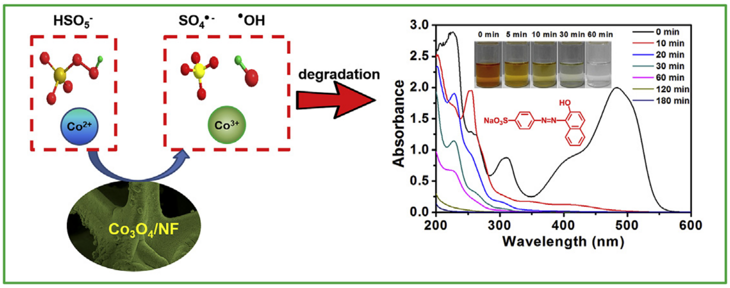
HIGHLIGHTS

- Novel Co_3O_4 nanowires and nanoflowers are supported on nickel foam (NF) surface.
- Co_3O_4/NF exhibits excellent capacity for peroxymonosulfate activation.
- Macroscopic Co_3O_4/NF can be easily and completely recycled with low cobalt leaching.
- Co_3O_4/NF shows remarkable reusability with stable performance.

GRAPHICAL ABSTRACT



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ABSTRACT

Cobalt-based heterogeneous catalyst has been recognized as one of most efficient activators for peroxymonosulfate (PMS) decomposition, but usually suffers from the poor stability and difficulty to recover and reuse. Here easily recyclable cobalt oxide (Co_3O_4) nanowires and nanoflowers grown on nickel foam (NF) are fabricated by a hydrothermal and calcination method. The prepared 3D Co_3O_4/NF catalyst is characterized and applied as a heterogeneous catalyst for PMS activation to generate sulfate radicals for decomposition of Acid Orange 7 (AO7). The results show that the AO7 degradation rate increases with cobalt loading and PMS dosage, but decreases with the increase of solution pH. The Co_3O_4/NF catalyst using 2 mM $Co(NO_3)_2 \cdot 6H_2O$ as cobalt source exhibits highest activity, and almost complete decolorization could be achieved within 30 min. The diverse effects of coexisting anions (SO_4^{2-}, HCO_3^-, NO_3^- and Cl^-) on AO7 degradation are observed and explained. After 10 consecutive runs, excellent catalytic reactivity of the catalyst remains while the level of leached cobalt during the catalyst usage is much lower than the maximum allowable concentration in drinking and natural water. More importantly, the macroscopic Co_3O_4/NF catalyst shows advantage of easy recycling after application compared to traditional catalysts.

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It is believed that the as-prepared Co_3O_4/NF is promising to be an effective and green heterogeneous catalyst for PMS activation to degrade organic pollutants for environmental application.

1. Introduction

Sulfate radicals ($SO_4^{\bullet-}$) based advanced oxidation processes (AOPs) are booming as promising and effective techniques for degrading refractory organic pollutants (Jaafarzadeh et al., 2017; Feng et al., 2017; Yuan et al., 2011). $SO_4^{\bullet-}$, with a higher standard reduction potential (2.5–3.1 V vs NHE) under neutral conditions than hydroxyl radicals (1.8–2.7 V vs NHE), has selective oxidation capacity and superior treatment performance over a wide pH range (Hu et al., 2017b; Huang et al., 2017). $SO_4^{\bullet-}$ can be generated via peroxymonosulfate (PMS) activation by transition metals, and cobalt ion (Co^{2+}) has been found to be the most effective activator for PMS decomposition (Zeng et al., 2015).

However, cobalt ion with high biological toxicity is recognized as one of priority metal pollutants and even possibly causes human carcinogen according to International Agency for Research on Cancer (IARC) (Guan et al., 2013; Shi et al., 2012). The discharge standard of cobalt is 1 mg/L for industrial wastewater based on GB/T 25467-2010 of China. The cobalt ions in the homogeneous Co^{2+}/PMS process could unavoidably lead to secondary pollution and cause health issues. Therefore, more attentions recently have been focused on PMS activation by heterogeneous cobalt sources, mainly including Co_3O_4 nanoparticles and cobalt supported on various nano/micro-materials (Deng et al., 2017; Fan et al., 2017; Saputra et al., 2013; Zeng et al., 2015; Zhang et al., 2017). For example, Saputra et al. (2017) prepared three different Co_3O_4 materials in sphere, cube and truncated cube and found that the catalytic activity for heterogeneous activation of PMS followed the order: Co_3O_4-cube > Co_3O_4-sphere > Co_3O_4-truncated cube. Hu et al. (2017a) synthesized Co_3O_4–Bi_2O_3 catalyst via microwave-assisted co-precipitation method and investigated its catalytic activity towards PMS activation for bisphenol A degradation. Lin and Chen, 2017 reported that Co and Co_3O_4 nanoparticles supported on a carbon matrix showed higher catalytic efficiency for caffeine degradation than unsupported Co_3O_4 nanocatalyst. Dou et al. (2016) investigated the performance of carbon spheres supported Co_3O_4 catalyst for the decomposition of methyl orange by PMS. Despite considerable success in improving the efficiency and stability of Co-based catalysts, additional separation and recovery steps, such as filtration, high-speed centrifugation or magnetic separation, are required to collect the highly dispersed catalysts because these nano/micro catalysts are usually prepared in the form of nano/micro powders. The high operational cost and the limited recovery rate of catalysts pose a key obstacle to practical application. Furthermore, in the actual operation process, the loss of active components during usage and low mass transfer ability due to the blockage of inner channels could also decrease catalytic activity. Thus, it is still challenging to develop novel synthetic strategies and catalyst support of Co_3O_4 for PMS activation.

Consequently, in this work we aim to introduce 3D macromaterials as Co_3O_4 support, which can be easily recoverable and reusable during complicated recycle processes. The 3D support should satisfy the following conditions at least: (1) large specific surface area and porosity for Co_3O_4 loading; (2) excellent mechanical property for multiple use; and (3) thermostability for Co_3O_4 preparation under hydrothermal and calcination condition. To the best of our knowledge, there are very limited materials that could meet all the above conditions. For example, carbon foam, although with large specific surface area, is not suitable due to its poor mechanical property. Recently, nickel foam (NF) with high porosity, robust ability, thermostability, mass transfer ability and especially 3D interconnected framework is considered as a new prospective catalyst support (Hui et al., 2013). Moreover, the NF supported catalyst can be made into certain shape and size during usage, and easily separated from liquid phase to ease the complicated recycle processes. Cai et al. (2014) successfully *in situ* decorated NF with Ni–Mn oxide nanosheets as 3D hierarchical monolith de-NOx catalysts via a simple hydrothermal reaction and calcination process. Very recently Zhao et al. (2017) reported 3D Fe–NiSe nanowires supported on nickel foam as a highly efficient, durable oxygen evolution catalyst. However, most of present studies on NF supported cobalt were focused on supercapacitors (Gao et al., 2010, 2016; Huang et al., 2012; Zhang et al., 2012; Zhu et al., 2015) or anode material for lithium ion batteries (Fu et al., 2012; Wang et al., 2014; Xu et al., 2013). To the best of our knowledge, NF-supported catalyst has not been applied to PMS activation in wastewater treatment. The conducting and porous 3D NF is supposed to not only serve as the physical support for Co_3O_4 nanostructure but also offer the channels for charge transport, which are beneficial for the maximum utilization of catalyst active sites (Xiong et al., 2014). Hence, the NF supported Co_3O_4 nanostructures would be envisaged as a novel and high efficient heterogeneous catalyst for the removal of organic pollutants from water.

Herein, we developed Co_3O_4 nanostructures on NF surface (Co_3O_4/NF) to form three-dimensional heterostructures via facile hydrothermal synthesis and calcination processes. The as-prepared Co_3O_4/NF composite was used as effective heterogeneous catalyst of PMS due to low cobalt leaching and easy recycling. Acid Orange 7 (AO7), a commonly used synthetic azo dye, was selected as a model pollutant. The influences of operational parameters including PMS amount, dosages of catalyst, initial solution pH values, reaction temperature and anions were investigated in terms of Co_3O_4/NF/PMS performance. The stability and reusability of the catalyst were demonstrated by reusing it in 10 successive experiments under the same reaction conditions.

2. Material and methods

2.1. Materials and reagents

Cobalt nitrate hexahydrate ($Co(NO_3)_2\cdot 6H_2O$) was purchased from Bodi Chemical Co. (Tianjin, China). Oxone ($KHSO_5\cdot 0.5KHSO_4\cdot 0.5K_2SO_4$, PMS), urea ($CO(NH_2)_2$), sodium chloride (NaCl), sodium sulfate (Na_2SO_4), sodium nitrite ($NaNO_3$) and sodium bicarbonate ($NaHCO_3$) were supplied by Aladdin Ltd. (Shanghai, China). Hydrochloric acid (HCl) and acetone (CH_3COCH_3) were obtained from Sinopharm Co. (Shanghai, China). AO7 was obtained from Sigma-Aldrich Co. (USA). Nickel foam (110 pores per inch (ppi), 380 g/m^2) was purchased from Changsha Lyrun Material Company (Changsha, China).

2.2. Preparation of Co_3O_4/NF catalyst

As illustrated in Fig. 1a, Co_3O_4/NF catalyst was prepared by