Science of the Total Environment 601–602 (2017) 99–108

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Cobalt super-microparticles anchored on nitrogen-doped graphene for aniline oxidation based on sulfate radicals

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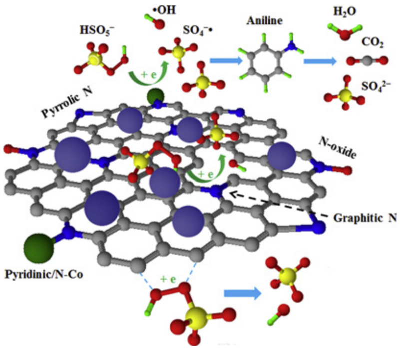
HIGHLIGHTS

- Co-NG was used as heterogeneous catalysts for PMS oxidation.
- Co-NG catalyst was found to poses the highest catalytic activity.
- The $SO_4^{-\bullet}$ and $^{\bullet}OH$ are the main radicals to degrade aniline.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 March 2017
Received in revised form 21 May 2017
Accepted 21 May 2017
Available online xxxx

Editor: D. Barcelo

Keywords:
Cobalt super-microparticles
Peroxymonosulfate
Sulfate radicals ($SO_4^{-\bullet}$)
Aniline

ABSTRACT

Cobalt super-microparticles anchored on nitrogen-doped graphene (Co–NG) were prepared using an inexpensive method and were tested for heterogeneous oxidation of aniline with peroxymonosulfate (PMS) in aqueous solutions. The crystal structure, morphology, and textural properties of Co–NG hybrids were investigated by various characterization techniques, such as X-ray diffraction, Raman spectroscopy, dark-field scanning transmission electron microscopy and X-ray photoelectron spectroscopy. Electron paramagnetic resonance and classical quenching tests were conducted to investigate the mechanism of PMS activation and aniline oxidation. The catalyst Co–NG exhibits an unexpectedly high catalytic activity in the degradation of aniline in water by advanced oxidation technology based on sulfate radicals ($SO_4^{-\bullet}$), and 100% decomposition can be achieved in 10 min. This paper offers new insights on heterogeneous catalysis.

1. Introduction

The quantity and toxicity of wastewater produced by processing industries, such as pharmaceutical factories, and urban waste are pernicious environmental issues. Both the growing population in developing nations and their rapid technological advances contribute to the increasing impact of this waste (Abdel-Raouf et al., 2012; Zhou et al., 2015). Organic pollution is highly hazardous and causes freshwater scarcity, ecosystem disruption, and increased public health hazards (Zhou et al., 2015). Due to these negative effects, the removal of pollutants from wastewater systems and the environment is of critical importance. Organic compounds are often resistant to natural degradation to the extent that traditional oxidization processes, such as biodegradation, can no longer produce satisfactory results. Intensive research interest has been directed to the development of advanced oxidation processes (AOPs) that are inexpensive, reusable, and adaptable to mass production.

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http://dx.doi.org/10.1016/j.scitotenv.2017.05.198
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Among the researched AOPs, H_2O_2 is the commonly used oxidant for degrading of organic contaminants in wastewater systems. H_2O_2 is converted to $HO^•$ free radicals in water to oxidize organic pollutants (Devi et al., 2016). However, the use of H_2O_2 has drawbacks that limit its widespread use: 1) sludge production during oxidation, which results in secondary pollution, 2) narrow pH requirement of 2–3, and 3) expensive storage and transportation of H_2O_2 (Zhou et al., 2015). As a result, peroxymonosulfate (PMS) is considered as a more efficient alternative to H_2O_2 due to its broad pH requirement and high redox potential (2.5–3.1 V). Furthermore, $SO_4^{-•}$ radicals have longer lifetime ($3–4 \times 10^{-5}$ s) than $HO^•$ radicals (2×10^{-8} s). In addition, the persulfate system has slower activation kinetics than the H_2O_2 system; it can be delivered at a considerable distance in the subsurface because of its stable properties, whereas H_2O_2 is difficult to deliver because of its high reactivity (Devi et al., 2016; Duan et al., 2015b; C. Wang et al., 2016; Y. Wang et al., 2014; Yao et al., 2012).

Graphene is a newly discovered material that acts as both a support and a catalyst. It has a single-layered structure, high electron mobility, excellent thermal stability, and high surface area that help disperse nanoparticles for advanced catalytic oxidation (Y-s. Wang et al., 2014). Doping the carbon network of graphene with adventitious heteroatoms (e.g., N, B, and P) introduces new active sites, increases the electrical conductivity as well as notably enhances the catalytic activity of graphene (Geng et al., 2011; Liang et al., 2012). In addition, several studies have shown that pairing graphene with a heteroatom, such as nitrogen, improves its catalytic ability (Duan et al., 2015b; C. Wang et al., 2016). As a result of the conjugation between the lone-pair of electrons on N element and the graphene *p* system, the incorporation of the N elements into graphene confers their unique electronic properties, which significantly enhances the number of active sites for advanced catalytic oxidation (Liang et al., 2012; Liu et al., 2010; Y-s. Wang et al., 2014). Wang et al. reported that N doped graphene (NG) completely oxidized 0.02 g/L aniline within 90 mins, exhibiting better catalytic efficiency than reduced graphene oxide (rGO) (C. Wang et al., 2016).

Due to the unique physical properties, graphene functions as either a free-metal catalyst through molecular engineering or a unique support for metal-based catalysts. Studies of graphene–metal interactions have shown that charge transfer can take place at the graphene–metal interface, and such charge transfer may be a major contributor to enhance the materials' catalytic activity (Yao et al., 2013). Numerous studies have shown that cobaltous can effectively activate PMS to degrade contaminants (Chan and Chu, 2009). However, the homogeneous Co^{2+}/PMS system has a major disadvantage in the toxicity of cobalt ions, since cobalt can cause several health problems such as asthma, pneumonia and other lung problems (Shukla et al., 2011). Several attempts have been made using Co as a heterogeneous catalyst for PMS activation (Yao et al., 2013; Zhou et al., 2015). Cobalt and nitrogen co-doped graphene (Co–NG) have shown superb capability in other industries, such as in hydrogen production (Fei et al., 2015). However, to our best knowledge, limited research on the efficiency of cobalt and nitrogen co-doped graphene as a chemical catalyst for PMS activation has been conducted.

Cobalt super-microparticles anchored on nitrogen-doped graphene as catalyst is a new research hotspot in the field of heterogeneous catalysis. The particle sizes of super-microparticles are between that of the atoms and microparticles. Compared with nano-catalysts, super-microcatalysts have many advantages: the active component can achieve greater dispersion, which can effectively improve the utilization of metals (especially precious metals); high activity, high selectivity and recyclability.

In this paper, we report an inexpensive and concise method to prepare Co–NG catalyst and its performance in catalytic degradation of aniline by PMS. The physical and chemical properties of Co–NG were evaluated using various techniques. The effects of the reaction conditions, such as catalyst dosage, PMS concentration, and reaction temperature on catalytic activity, reaction kinetics and degradation mechanism have been investigated. Co–NG was found to have potential applications in wastewater treatment.

2. Materials and methods

2.1. Materials

PMS, available as a triple salt of sulfate commercially known as Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, 4.5% to 4.9% active oxygen), was obtained from Shanghai Ansin Chemical Co. Ltd. and used as an oxidant. Aniline ($C_6H_7N_2$, 99.99%) was obtained from Shanghai Aladdin Reagent Co. Ltd. Cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$), methanol (CH_3OH), and sodium nitrate ($NaNO_3$) were provided by Sinopharm Chemical Reagent Co., Ltd. (China). Other reagents, including sulfuric acid (H_2SO_4), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2), and hydrochloric acid (HCL) were provided by Shanghai Junhui Chemical Co., Ltd. (China). All of these chemicals were used as received without any further purification.

2.2. Synthesis of catalysts

Graphene oxide (GO) was prepared using the modified Hummers Method (Sergi et al., 2014). In a typical synthesis, an aqueous suspension of GO was first obtained by sonicating 100 mg of GO and 50 mL of deionized water for 3 h, and then 10 mL of $CoCl_2 \cdot 6H_2O$ (3 mg/mL) was added to the suspension. The mixture was sonicated for another 10 min and freeze dried for over 48 h to produce a dry brownish powder that was subsequently placed in a quartz tube furnace. After purging the system with Ar thrice, the temperature was increased to 750 °C at 20 °C/min in an Ar (150 s.c.c.m.) and NH_3 (50 s.c.c.m.) atmosphere. The reaction proceeded for 1 h before cooling the catalyst to room temperature under Ar protection, and the final product Co–NG with a blackish color was obtained.

The control sample Co–G was prepared with the same procedure except that NH_3 was not introduced during the annealing process; the control sample NG was prepared with the same procedure except that $CoCl_2 \cdot 6H_2O$ was not added.

2.3. Characterization and analytical techniques

X-ray diffraction (XRD) was performed to investigate the structure of catalysts using Ultima IV X-ray diffractometer with Cu Kα ($\lambda = 1.5418$ Å) radiation, a voltage of 40 kV, and a current of 40 mA with a scanning speed of 0.01°/s from 5° to 85° (2θ). The structural composition was detected by X-ray photoelectron spectroscopy (XPS) using ESCALAB 250 photoelectron spectrometer (Thermo VG Scientific, USA) with Al Kα (1486.6 eV) as the X-ray source. Dark-field scanning transmission electron microscopy (DF-STEM) was performed to investigate the morphology of the catalysts using a Zeiss Neon 40 EsB FIBSEM. The sample was prepared by dispersing a small amount of dry powder in ethanol. Electron paramagnetic resonance (EPR, Bruker) was applied to probe the radical generation process during PMS activation, and the reactive radicals were trapped by 5,5-dimethylpyrroline-oxide (DMPO, 0.1 M). The EPR instrument was operated at the center field of 3514.8 G, sweep width of 100.0 G, and power of 10 mW with sweeping time of 30 s. The total organic carbon (TOC) of the solutions was measured after immediate quenching with excessive $NaNO_2$ using a Shimadzu TOC-VCPH analyzer to evaluate the mineralization of the organics during oxidation. The leached Co^{2+} ion concentration as measured by inductively coupled plasma (ICP, Leeman, Teledyne) to determine the metal ion concentration in the solution, identify, and differentiate the metal ions down to ppb levels. The solution was obtained during the reaction, filtered and mixed with 2% nitric acid aqueous solution before analysis.