

Photochemical oxidation of phenol solutions using Co₃O₄ nanorods

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Introduction

Cobalt-based catalysts have been widely used in energy and environmental applications.^{1,2} Cobalt ions, cobalt oxide nanoparticles and supported cobalt catalysts are able to activate Oxone[®] (peroxymonosulfate, PMS) to produce sulfate radicals (SO₄^{•-}), which have a higher oxidation potential and a wider solution pH range than hydroxyl radicals (OH[•]). The produced radicals will drive advanced oxidation processes (AOPs) to decompose organic pollutants to inorganic ions, CO₂ and H₂O for wastewater remediation. PMS can also be activated by heat, UV or electrons.³

Co₃O₄ was recently demonstrated as an efficient photocatalyst for H₂ production from water/ethanol solution.⁴ It would be interesting to discover if the photoinduced carriers (e⁻/hole) can promote the activation of PMS for producing more sulfate radicals.

This study reports the synthesis of Co₃O₄ nanorods at different temperature. Their performances in catalytic oxidation and photochemical oxidation of phenol solutions were investigated. The mechanism of enhanced efficiency from combination of photocatalysis and chemical oxidation were discussed.

Materials and Methods

Cobalt (II, III) oxide, Co₃O₄ nanorods were prepared by a complex-pyrogenation method using cobalt nitrate as cobalt precursor.⁵ In a typical procedure, 3.6 g of Co(NO₃)₂•6H₂O was dissolved in 40 mL water. Then 20 mL of 30% ammonia solution was slowly added into the cobalt nitrate solution with stirring. The precipitate was filtered and mixed in 10 mL H₂O₂, then 70 mL ultrapure water was introduced. After stirring for 30 min, the suspension was transferred into a 125 mL Teflon-lined autoclave and the heated in an oven at 75 °C for 3 h. After washing and drying, the precipitate was further heated at 200, 250, 300, 350, and 400 °C, respectively and denoted as CN-200, CN-250, CN-300, CN-350, and CN-400. The physicochemical properties of the samples were analyzed by a variety of characterization techniques, such as X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), transition electron microscopy (TEM), nitrogen sorption isotherm, and X-ray photoelectron spectroscopy (XPS). Performance of PMS activation of the catalysts was evaluated by catalytic oxidation of 20 ppm phenol solutions. Photochemical oxidation ability was investigated by introduction of light irradiations to the chemical oxidation. The concentration of phenol was monitored by a high-performance liquid-chromatography (HPLC).

Results and Discussion

It was found that the calcination temperature would significantly affect the catalytic performance of the Co₃O₄ nanorods. For the sample annealed at 200 °C, almost 100% phenol removal was made within 90 min. While for the sample from 400 °C, 180 min was required.

The sample prepared at 300 °C, CN-300 was selected to conduct photochemical oxidation of phenol. Figure 1 (B) shows that CN-300 was not able to effectively degrade phenol by photocatalysis only. Experiments showed that with the assistance of light, the phenol removal was significantly improved. It was expected that an oxidant can effectively capture carriers for oxidation reactions. When the Oxone[®] loading was 1.0 g/L, 2.2 times enhancement was achieved.

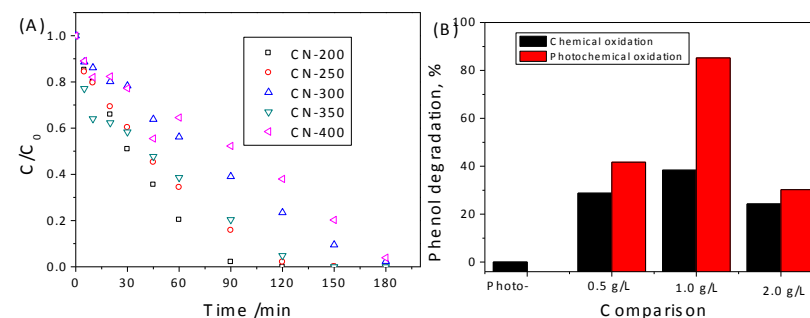


Figure 1. (A) Catalytic oxidation of phenol over Co₃O₄ nanorods prepared at different calcination temperature. [Solution volume: 500 mL; Catalyst: 0.2 g/L; Phenol: 20 ppm, Temperature: 25 °C; PMS: 2 g/L] (B) Chemical oxidation and photochemical oxidation of phenol at a time interval of 45 min. Catalyst loading of 0.2 g/L.

Significance

The photoinduced electron/hole pairs on Co₃O₄ nanorods can be captured by Oxone[®] to conduct photochemical oxidation of phenol solutions. Therefore, solar energy was utilized for waste water treatment.

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