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Enhanced degradation of organic pollutants over Cu-doped $LaAlO_3$ perovskite through heterogeneous Fenton-like reactions

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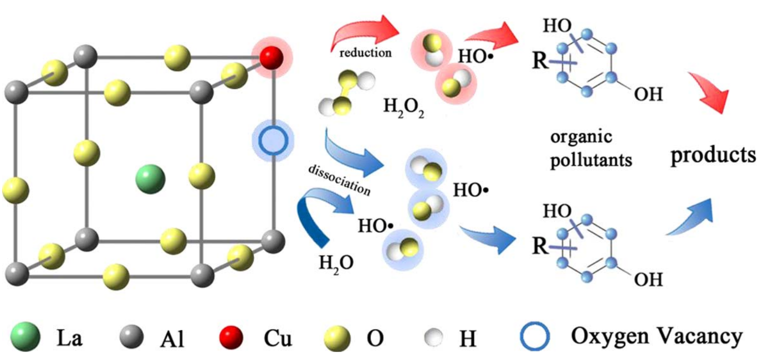
GRAPHICAL ABSTRACT



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ABSTRACT

Cu-doped $LaAlO_3$ perovskite ($LaAl_{1-x}Cu_xO_3$) was synthesized via a Pechini-type sol–gel process for the oxidative degradation of persistent organic compounds. The characterization results show that Cu was incorporated into the structure of sphere-like $LaAlO_3$ and formed the bond of La/Al—O—Cu. $LaAl_{0.95}Cu_{0.05}O_3$ performed excellent activity and stability for the degradation and mineralization of various organic pollutants through heterogeneous Fenton-like reactions. In the practical reaction process, at the organic pollutant initial concentration of 25 mg L^{-1}, 1.0 mol H_2O_2 produces 1.8 mol $HO^{\cdot}$ radicals within 60 min and 1.0 mol H_2O_2 still produces 1.3 mol $HO^{\cdot}$ radicals after reaction time of 240 min. The results of ESR and active species trapping experiments indicated that $HO^{\cdot}$ radicals acted the dominant role during the degradation of pollutants in $LaAl_{0.95}Cu_{0.05}O_3/H_2O_2$ system. Combining with in-situ Raman analysis and the XPS results of $LaAl_{0.95}Cu_{0.05}O_3$ before and after reaction, H_2O_2 was predominantly reduced to $HO^{\cdot}$ on the electron-rich Cu center, and H_2O_2/H_2O can be dissociated on oxygen vacancies (OVs) to enhance formation of $HO^{\cdot}$ on the surface of $LaAl_{0.95}Cu_{0.05}O_3$, resulting in the high catalytic activity of $LaAl_{0.95}Cu_{0.05}O_3$. This efficient material can potentially be used as a promising catalyst for the efficient degradation of organic pollutants in environmental pollution cleanup.

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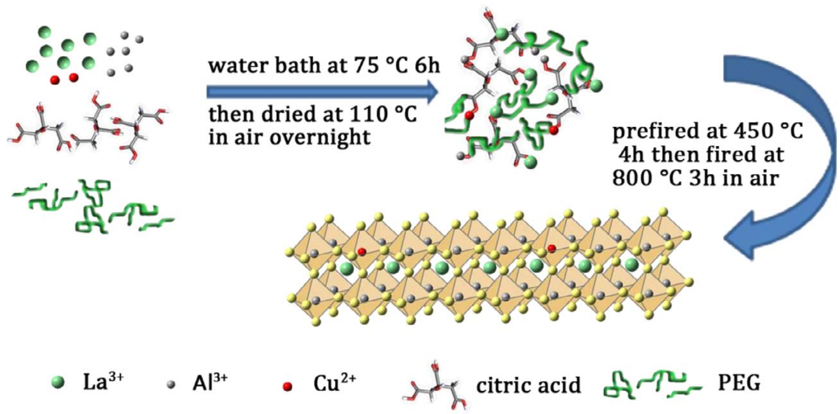

Fig. 1. The schedule illustration of the synthesis processes.

1. Introduction

With the rapid development of chemical industry, different kinds of persistent aromatic pollutants, such as phenols, pesticides, pharmaceuticals, endocrine disruptors, were produced and unavoidably released into the natural environment, which could cause serious environmental effects and biohazard [1]. During the past few years, many researchers have focused on the efficient elimination of organic pollutants from aqueous solutions, and various techniques have been adopted such as adsorption [2,3], flocculation [4,5], Advanced Oxidation Processes (AOPs) [6–8] and bio-contact oxidation [9]. Among these methods, AOPs as a useful technique for dealing the persistent pollutants has been widely applied in the treatment of industrial wastewater. The strong chemical species ($HO^{\cdot}$, $HO_2^{\cdot}$, etc.) generated from AOPs [10–12] are highly reactive and can mineralize most organic substances into inorganic compounds and small molecules.

As one of AOPs, the classic Fenton reaction has attracted worldwide attention recently due to its high performance, simplicity and environmental friendly [13–15]. However, the widespread application of Fenton reaction is still limited by the narrow working pH range (pH = 2.5–3.5), the production of sludge (mainly iron-containing, a secondary pollutants) and the catalyst lost continuously. In addition, heterogeneous catalysts still neutral and acidic conditions were more effective. However, in many cases, industrial effluents are formed at basic pH conditions [16]. Therefore, it is essential to develop highly active and stable Fenton catalysts at extensive pH range. It is well known that perovskite-type oxides (ABO_3) have been applied to industrial reactions as important heterogeneous catalysts [17–19]. With the high tolerance factor, various sizes of cations can be dissolved in both A- and B-site cation sublattices. Consequently, oxygen vacancies (OVs) are generated to compensate the charge of substituting ions [20]. $LaAlO_3$ as a combination of rocksalt-LaO with rutile-AlO_2 structure has attracted the intense interest of the scientific society [21].

Recently, different kinds of Cu-based materials have been synthesized extensively in the field of catalysis, especially as Fenton catalysts, such as Cu-doped metal oxide [22,23], Cu-doped goethite [24] and Cu-doped magnetic porous carbon [25]. While the utilization efficiency of H_2O_2 ranged from 10% to 60% in Cu-based systems were reported [26]. Meanwhile, different kinds of perovskite materials have been studied as Fenton catalysts, such as a series of $LaBO_3$ perovskites (B = Ti, Fe,) [27,28], the influence of the A-site cation in $AFeO_3$ (A = La, Bi) perovskite-type oxides [29,30] and a mesoporous SBA-15 host support for the perovskite [31,32]. However, to gain applications in practice and the catalytic efficiency of these oxides have to be improved. Therefore, the H_2O_2 utilization efficiency has to be enhanced and the formation rate of hydroxyl radicals ($HO^{\cdot}$) has to be accelerated during the Fenton reaction process, which is critical to increase the catalytic efficiency of Fenton reaction.

Herein, the Cu-doped $LaAlO_3$ perovskite catalyst was successfully synthesized by a sol–gel route. Several ubiquitous aromatic pollutants, including phenol, pharmaceuticals (such as diphenhydramine (DP), ciprofloxacin (CIP), ibuprofen (IBU), and phenytoin (PHT)), pesticides (such as 2-chlorophenol (2-CP), 2,4-dichlorophenoxyacetic acid (2,4-D)), and endocrine disrupting chemicals (such as bisphenol A (BPA)), were selected as representative pollutants to evaluate the oxidation degradation activity of the catalyst under different experimental conditions. The catalyst was characterized by high-resolution transmission electron microscopy (HRTEM), field emission scanning electron microscope (SEM), X-ray diffraction (XRD), The Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and extended X-ray absorption fine structure (EXAFS) spectroscopy. Additionally, the interaction processes between $LaAl_{0.95}Cu_{0.05}O_3$ and hydrogen peroxide (H_2O_2) were detected by electron spin resonance (ESR) and in-situ Raman spectroscopy, and a complex mechanism of Cu-doped $LaAlO_3$ ($LaAl_{1-x}Cu_xO_3$) heterogeneous Fenton-like reactions was proposed from the analytical results.

2. Experimental

2.1. Reagents

Eight contaminants (phenol, DP, CIP, IBU, PHT, 2-CP, 2,4-D and BPA) were purchased from Acros (Geel, Belgium). Lanthanum nitrate ($La(NO_3)_3{\cdot}6H_2O$), aluminium nitrate ($Al(NO_3)_3{\cdot}9H_2O$), copper nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$) and H_2O_2 (30%, w/w) were purchased from Sinopharm Chemical Reagent Co., Ltd. Citric acid and polyethylene glycol (PEG, molecular weight = 10000) were obtained from Beijing Chemical Co. Ltd. 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO) was supplied by Sigma Ltd. All chemicals were analytical grade.

2.2. Catalyst synthesis

$LaAl_{1-x}Cu_xO_3$ perovskite (x = 0.0–0.1) composites were synthesized via a Pechini-type sol–gel process (Fig. 1). In a typical procedure [33,34], the required amounts of $La(NO_3)_3{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ and $Cu(NO_3)_2{\cdot}3H_2O$ were dissolved in 20 mL solvent (ethanol: deionized water = 7:1). Thereafter, citric acid and PEG were added into the nitrate precursors as the chelating agent and the molar ratio of the citric acid and metal ions was 2:1. The resultant mixtures were stirred for 1 h at room temperature and condensed at 75 °C in a water bath for 6 h to evaporate water until dry gels formed, and then dried at 110 °C overnight. The gels were well ground and prefired at 450 °C for 4 h. Thus treated samples were fully ground and fired at 800 °C for 3 h. The x values of initial synthesis mixtures were fixed to 0, 0.01, 0.02, 0.05 and 0.1.