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Enhanced generation of hydroxyl radicals on well-crystallized molybdenum trioxide/nano-graphite anode with sesame cake-like structure for degradation of bio-refractory antibiotic

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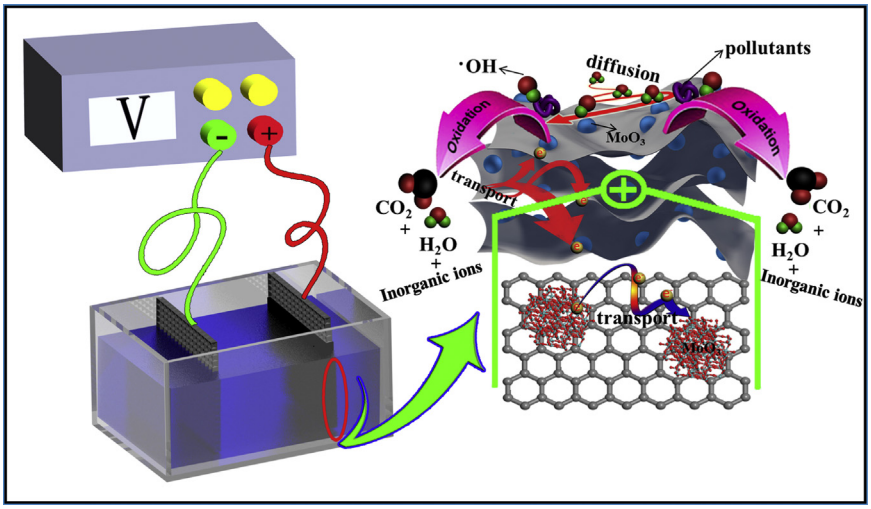
GRAPHICAL ABSTRACT



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ABSTRACT

Anodic electro-catalysis oxidation is a highly effective way to solve the pollution problem of antibiotics in wastewater and receiving water bodies. In this study, for the first time, molybdenum trioxide/Nano-graphite (MoO_3/Nano-G) composites are synthesized as anodic catalysts by a surfactant-assisted solvothermal method followed by low-temperature calcination. The effects of the proportion of MoO_3 to Nano-G (10, 30 and 50%) on the properties of composites are investigated through structural characterizations and electrochemical measurements. Results indicate that MoO_3(30)/Nano-G electrode displays the electro-catalysis degradation efficiency of 99.9% towards ceftazidime, which is much higher than those of Nano-G (46.7%) and dimensionally stable anode (69.2%). The degradation mechanism for ceftazidime is studied by investigating the yields and kinds of active species. Results show that all of the ·OH, $\cdot O^{2-}$ and H_2O_2 are responsible for the electro-catalytic degradation process, and the produced

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Hydroxyl radicals
MoO_3/nano-ganode
Refractory organic wastewater

·OH radicals are the major active species for ceftazidime degradation. The synergistic effects between MoO_3 and Nano-G greatly contribute to the activation of H_2O molecules to produce ·OH, meanwhile the special sesame cake-like structure facilitates to the exposure of contaminants to ·OH on active sites to enhance the degradation efficiency. These results suggest that MoO_3/Nano-G electrodes can be considered as the promising catalysts for treating bio-refractory organic wastewater.

1. Introduction

Antibiotics have been widely used in medical treatment, livestock and poultry breeding and food industry, etc, because it can effectively inhibit and/or kill the mycoplasma, chlamydia, spirochetes, rickettsia and other pathogenic microorganisms [1]. The sources of antibiotics are widely distributed in environment, including the pharmaceutical factory, urban domestic sewage, livestock and poultry breeding wastewater, hospitals and biological treatment residues in wastewater treatment plants [2]. In general, the most-commonly used technologies for purifying wastewater are the biological treatments [3]. However, most of the antibiotics in wastewater are difficult to be removed completely (or even cannot be) by biological treatments due to their polycyclic complex structures and toxic effects on microorganisms in aqueous solutions, that is why more and more antibiotics are found in the drainage of sewage treatment plants [4–6]. For example, ceftazidime, as a widely used cephalosporin antibiotic due to its wide antibacterial spectrum, strong antibacterial activity and high efficiency, has an important position in the anti-infective drugs market [7]. However, the trace amounts of ceftazidime in the environment can bring severe influence via a long-term accumulation, because it can not only cause serious harm to humans, but also generate toxic effects for other living beings [8]. Hence, it is necessary to develop a promising technology for the removal/degradation of ceftazidime with low concentration in the environment.

Recently, advanced oxidation processes (AOPs), such as photocatalysis [9], photoelectro-catalysis [10] and electro-catalysis [11], have been regarded as the excellent and effective approaches for the degredation of bio-refractory organic wastewater [11–13]. Especially, the electro-catalysis, which can in-situ produce strong oxidizing free radicals (e.g. hydroxyl radicals (·OH), anode) and hydrogen peroxide (H_2O_2 (·OH), cathode) on the surface of electrodes, has the characteristic of low requirement to the equipment and reaction condition for degradation and/or mineraliziation of antibiotics contaminants [14,15]. Lately, it is reported that the electro-oxidation of organics can be smoothly implemented on some anode materials such as dimensionally stable anode (DSA) [16], lead dioxide (b-PbO_2) anode [17] and conductive diamond anode (CDA) [18]. Among them, the DSA is a traditional electrode material for the electro-oxidation removal of pollutants on account of its chemical stability, low cost and long lifetime [19]. However, it has been proved in our previous studies that the nano-graphite (Nano-G) electrode has better anodic oxidation performance than that of the DSA electrode for antibiotics degradation [20,21]. The Nano-G material, which possesses unique properties such as high electron mobility, enough specific surface, large surface energy, etc, has attracted a lot of attentions in recent years [20,22]. But, the application of Nano-G is still limited by some shortcomings, such as electrical disconnection, structure transformation, etc [23,24].

In recent years, metal-oxide semiconductors (such as WO_3 [25], SnO_2 [26], MnO_2 [15] and MoO_3 [27,28]) are introduced in electrochemistry fields as electricatalytic active materials on account of their environmentally friendly characteristic, nontoxicity, high stability and good catalytic activity. Particularly, MoO_3 with a special structure of Mo^{6+} kept in an octahedral oxygen environment has a high capacity for desorbing surface oxygen to form sufficient surface oxygen vacancies [29], which can energetically enhance the electron transport on MoO_3 surface [30,31]. Nevertheless, the application of MoO_3 is greatly restricted by its poor electrical conductivity and low surface area. Recently, a lot of promising supports, such as carbon [32], polypyrrole [33], reduced graphene oxide [34], have been composited with MoO_3 to overcome these defects. Therefore, the Nano-G can be considered as a promising support for MoO_3 (MoO_3/Nano-G). On the one hand, Nano-G can greatly improve the bad conductivity and avoid the agglomeration of nano-sized MoO_3 to increase active sites on MoO_3/Nano-G. On the other hand, the defect bands originating from the defects in MoO_3, such as oxygen vacancies, may exist within the energy band of MoO_3, which can allow the effective transport of holes through the MoO_3 to Nano-G [35]. These synergistic effects between MoO_3 and Nano-G may greatly contribute to the geneation of ·OH to enhance the degradation efficiency of pollutants. To the best of our knowledge, the electro-catalysis degradation of antibiotics by using MoO_3 and Nano-G based electrodes has not yet been reported.

In this study, MoO_3/Nano-G composites are prepared by using a surfactant-assisted solvothermal process followed by a low-temperature calcination method. The MoO_3/Nano-G electrodes used for electro-catalysis degradation are prepared by hot-press approach. With the uniformly dispersed MoO_3 nanoparticles as the active components and the Nano-G as the conductive carrier, the contact resistances (between MoO_3 and Nano-G) of the resulting composites are expected to be efficiently reduced. The optimum proportion of MoO_3 to Nano-G in the composites is investigated through structural characterizations and electrochemical measurements. Performances of the as-prepared MoO_3/Nano-G electrodes for degradation of organic wastewater (ceftazidime as the representative antibiotic) are also explored. As expected, the MoO_3/Nano-G electrode with the sesame cake-like structure should exhibit high electro-catalysis activity and durability. The relationships between the assembled structure and the catalytic activity of MoO_3/Nano-G are discussed. Moreover, the enhanced catalytic degradation behaviors and mechanisms are also proposed.

2. Experimental design

2.1. Reagents and materials

All of the chemicals and solvents were of analytical grade without any further purification in this study. Ammonium molybdate, nitric acid, ethanol, isopropano and sodium sulfate were purchased from Sinopharm chemical reagent co., Ltd (China). Polyvinylpyrrolidone (PVP) as the surfactant was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. The Nano-graphite (12,500 mesh) was purchased from Xiang Yang graphite products processing plant in Guangdong province, China. Ceftazidime was purchased from Harbin General Pharmaceutical Factory's Sale Company and its molecular formula was shown in Fig. S1. Deionized (DI) water was used throughout the experiments.