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Fabrication of Fe-doped birnessite with tunable electron spin magnetic moments for the degradation of tetracycline under microwave irradiation

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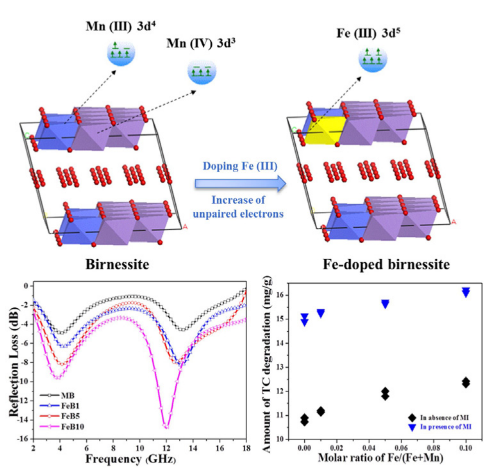
HIGHLIGHTS

- Fe-doped birnessites could be used as a catalyst for tetracycline degradation under microwave irradiation.
- The increase of unpaired electrons in Fe-doped birnessites resulted in higher electron spin magnetic moment.
- The dielectric loss was the main factor to improve the microwave absorption performance.
- Microwave absorption performance could be improved by controlling the electron spin magnetic moment of the birnessite.

GRAPHICAL ABSTRACT



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ABSTRACT

Manganese oxides exhibit an excellent microwave absorption performance that could increase the degradation efficiency of organic pollutants in contaminated water. Incorporation of various transition metals into manganese oxides could bring about changes in their crystal structure and improve their physicochemical performance. In this work, a better microwave absorption material was obtained by adjusting and controlling the electron spin magnetic moments of Fe-doped birnessite. The powder X-ray diffraction, inductive coupled plasma emission spectrometer, X-ray photoelectron spectroscopy, and network analyses were performed to characterize the crystal structure, chemical composition, valence and content of the elements, and the microwave absorption performance of the obtained samples. Doping Fe into birnessite resulted in little changes to their crystal structure. The narrow energy spectrum of Fe (2p) revealed that the doped Fe was in the form of Fe (III) in birnessite structure. As the content of Fe (III) increased, the content of Mn (III) decreased accordingly. Substitution of Mn (III) by Fe (III) in the birnessite crystal lattice, confirmed by combining the characterization analyses with structure refinements for each doped

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sample, increased the overall numbers of unpaired electrons in birnessite structure, resulting in a higher electron spin magnetic moment and better microwave response. Compared with the non-doped sample, Fe-doped birnessite improved the efficiency of tetracycline degradation, which proved that Fe-doped birnessite indeed had better response towards the microwave, and thus, could be utilized for better removal of organic pollutants under microwave irradiation.

1. Introduction

Birnessite, as a common manganese oxide mineral, has drawn extensive attention in recent years due to its stable layer structure and distinctive physicochemical properties [1]. Although it has a complicated chemical composition that mainly consisted of trivalent and tetravalent manganese, the basic unit of its structure is [MnO_6] octahedra, which are connected among the layers by edges [2,3]. Owing to the replacement of Mn (II) and Mn (III) for Mn (IV), exchangeable cations such as Na^+, K^+, and Mg^{2+}, as well as water molecules, are incorporated into its structure, occupying the interlayer regions to compensate the charge deficiency and resulting in a d_{001} spacing close to 0.700 nm [4]. As a result of differences in types of interlayer exchangeable cations, valances of Mn in birnessite structure, and large specific surface area, birnessite exhibits excellent ion exchange and redox performance in many chemical reaction processes. Therefore, birnessite materials have been widely used as adsorbent and catalysis [5–7].

On account of the similar effective ionic radii, ionic charges, and crystal field environment between the transition metals and central Mn in [MnO_6] octahedra, Mn in the crystal lattice could be commonly substituted in most of manganese minerals, which has been proven as an effective way to change or improve certain properties of manganese oxides (MOs) by doping varieties of transition metal elements [8–10]. For instance, doping Co into birnessite could dramatically improve the capacity retention and discharge-recharge performance in novel Li ion batteries [11]. Co-doped birnessite also showed a better catalytic oxidation performance in the oxidation of petroleum wax [12]. A latest study demonstrated that Ni-doped birnessite exhibited a large decrease in crystallinity with a significant increase in specific surface area, and an increase in the average oxidation state of Mn, which played an essential role in improving oxidation of As (III), in comparison to the original birnessite [13]. In contrast, Fe-doped hexagonal birnessite lowered the number of stacking layers and the average oxidation state of Mn with part of the Fe doped into the layer structure and the rest retained in the interlayers [14]. These studies mainly focused on the preparation and characterization of doped birnessite as well as the influence of doping on their properties. However, few reports discussed the relation between the crystal structure and performance.

MOs play a significant role in catalytic oxidation of organic pollutants under the microwave irradiation, which undoubtedly make them excellent microwave absorption materials [15]. MOs could release a vast amount of heat and generate a stronger reactive center in the presence of microwave irradiation, contributing to the enhanced removal of organic pollutants from the wastewater [16,17]. Furthermore, it was speculated that the catalytic oxidation performance of MOs was mainly attributed to the mixed valances of Mn in [MnO_6] octahedra [18]. Under microwave power of 400 W and pH 1, the tetracycline removal efficiency reached up to 97.0% in the presence of 0.2 g akhtenskite and 50 mL of 50 mg/L TC solution in 30 min [19]. As for birnessite, methylene blue was almost eliminated thoroughly under microwave irradiation at 400 W with static adsorption for 5 h [20]. A further study deduced that due to the presence of various valences of Mn in [MnO_6] octahedra, MOs could produce different electron spin magnetic moments, which had a great impact on the removal of methylene blue, and a larger spin magnetic moment promoted the catalytic oxidation process by comparing the birnessite with akhtenskite [21]. Nevertheless, these reports added much importance to the degradation of organic pollutants by the pristine birnessite under microwave irradiation, few of them studied the degradation pathway of contaminants by doped birnessite and the effects of controllable electron spin magnetic moments on microwave absorption performance.

Tetracycline (TC) is one of the mostly used antibiotics in human and animals. Due to its poor absorption by animals and human beings and low degradation rate, it was persistent in the environment [22]. As such, significant amounts of work were dedicated recently to the studying of improving the TC removal from water. Previous studies showed that TC could be effectively photocatalytically oxidized in aqueous suspension of TiO_2 or ZnO [23]. However, the presence of humic acid could inhibit the TC oxidation under UV in the presence of TiO_2 as the catalyst [24]. Persulfate activation in combination with UV irradiation could also increase the TC degradation efficiency [25]. Besides, in the presence of activated carbon coated with nanoscale Fe_3O_4 as the catalyst and pursulfate as the oxidant, the TC removal efficacy could reach up to 99.8% [26]. Using goethite as a catalyst, ultrasound enhanced ozonation of TC [27]. Similarly, Fenton-like degradation of TC using magnetite as a catalyst could also be enhanced under ultrasonication [28]. However, these methods could often produce adverse effects on the environment and bring secondary pollution [29]. Therefore, it is of great meaning to improve the TC removal efficiency by adopting some new technologies or materials. Due to the excellent catalytic oxidation performance and environmentally friendly of the birnessite materials, they are selected as the proper candidates.

In this work, a series of Fe-doped birnessites were synthesized by hydrothermal method. They were then tested for TC degradation under different reaction time and power in the presence of microwave irradiation. Owing to the tunable electron spin magnetic moments of Fe-doped birnessite, a better microwave absorption performance was obtained. In our perspective, due to the close connection between structure and performance, it is of great value to understand the interaction of MOs with Fe and its impact on microwave absorption performance, which will help us develop a new way to prepare better microwave absorption materials.

2. Materials and methods

2.1. Materials

Reagents used for preparing birnessite were $KMnO_4$, $MnCl_2 \cdot 4H_2O$, NaOH, and $FeCl_3 \cdot 6H_2O$, and all of them were purchased from Beijing Chemical Industry with a purity above 99.97%. The TC used in the experiment was provided by Hefei Bomei Biological LLC. All aqueous solutions were prepared in distilled water.