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Engineering birnessite-type MnO_2 nanosheets on fiberglass for pH-dependent degradation of methylene blue

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ABSTRACT

We construct hierarchical MnO_2 nanosheets @ fiberglass nanostructures via one-pot hydrothermal method without any surfactants. The morphology and structure of MnO_2-modified fiberglass composites are examined by focus ion beam scanning electron microscopy (FIB/SEM), X-Ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR). The birnessite-type MnO_2 nanosheets are observed to grow vertically on the surface of fiberglass. Furthermore, the birnessite-type MnO_2-fiberglass composites exhibit good ability for degradation of methylene blue (MB) in different pH levels. In neutral solution (pH 6.5–7.0), it achieves a high removal rate of 96.1% (2 h, at 60 °C) in the presence of H_2O_2; and in acidic environment (pH 1.5), 96.8% of MB solution (20 mg/L, 100 mL) is decomposed by oxidation within only 5 min. In principles, the rational design of MnO_2 nanosheets-decorated fiberglass architectures demonstrated the suitability of the low-cost MnO_2-modified fiberglass nanostructure for water treatment.

1. Introduction

Manganese dioxides (MnO_2) have attracted considerable interest due to their distinctive physical, inexpensiveness, chemical properties and wide applications in catalysis [1,2], oxidation [3], sensor [4], supercapacitor [5] and so forth, and some reports have demonstrated that MnO_2 is one of the outstanding candidates for the practical application in the degradation of dye wastewater in different surroundings. Among them, the birnessite-type MnO_2 (δ-MnO_2) exhibits a larger adsorption and catalytic capacity than other manganese compounds [6,7]. This is due to δ-MnO_2 consists of a kind of two-dimensional lamellar structure that formed by [MnO_6] octahedral sharing edges, and its interlayer can underwent cation exchange reactions [8]. At present, lamellar structures of birnessite-type MnO_2 nanosheets have been prepared by the electrochemical and chemical routes, and their performance in wastewater treatment application have been investigated [9,10]. However, these methods suffer from complicated or strict conditions, and it remains a challenge to develop facile and economic synthetic methods for MnO_2 nanosheets-based composites.

An emerging attractive approach to improve the degradation of MnO_2 materials is to grow smart integrated nanostructure with a high surface area. Among supporting materials (glass, cement, red brick and inorganic fibers), fiberglass is economical, flexible, corrosion resistant and easy to handle [11]. Fiberglass materials have often been used to reinforce the mechanical property of the material including strength and stiffness, enhance wear or erosion resistance [12–14]. Recently, great interest has been expressed by researchers in functional modification based on fiberglass materials [15–18]. Various thin films of materials have been coated on fibers including polymers, metals, metal oxides, charged molecules, as well as nanomaterial and composites of combinations of metal, polymers, dyes, and biomaterial. It is found that the highly active states of supported components can be formed on fiberglass supports under certain conditions. This can be due to the specific structure of fiberglass and to the localization of supported materials in them.

In this work, we fabricated novel MnO_2-modified fiberglass composites via hydrothermal treatment without any organic auxiliary agent. The obtained MnO_2-modified fiberglass composites were employed as catalysts or oxidants for degradation of MB (a detailed illustration was shown in Scheme 1). MnO_2-modified fiberglass composites exhibit good performance for the degradation of MB at different pH values solution, which implies its good potential in the application of wastewater treatment.

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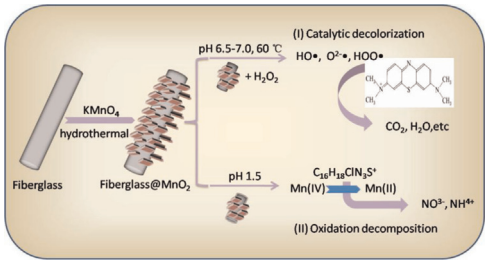

Scheme 1. Synthesis of MnO_2-modified fiberglass composites by means of the hydrothermal method as well as their application for the degradation of MB.

2. Experimental details

2.1. Materials

All the chemical reagents were purchased from Alfa Aesar, which were of analytical purity and used without any further purification. The fiberglasses employed were provided by Chongqing Polycomp International Corporation (CPIC).

2.2. MnO_2-modified fiberglass preparation

The MnO_2-modified fiberglass composites were successfully prepared without any surfactant by a facile method. In a typical synthesis, raw fiberglass (60–100 mg) was dispersed into the $KMnO_4$ solution (30 mL, 0.01 M) to form a mixture, and then, the mixture was put into a Teflon-lined stainless steel autoclave and stirred for 30 min. Afterwards, mixed solution was treated under 160 °C for 24 h. Finally, the resulting sample was collected, washed with distilled water, and dried at 60 °C for 8 h. Furthermore, the synthesis process can scale up to a larger yield (1.0 g) of MnO_2-modified fiberglass composites in a 0.3 L reaction system. In order to elucidate the effect of processing time on catalytic performance of composites, as-prepared samples at 160 °C for 4 h and 12 h were collected respectively.

2.3. Materials characterization

The crystallographic information and chemical composition of as-prepared products were analyzed powder X-ray diffraction (Rigaku D/max-2500 with Cu K_α radiation) and Fourier transform infrared spectroscopy (FTIR, Nicolet 5DXC). The morphology of the raw fiberglass and the MnO_2-modified fiberglass composites were carried out with focused ion beam (Zeiss Auriga FIB/SEM). Absorption spectrum was measured with ultraviolet – visible light (UV–vis) spectrophotometer (Model UV-2450, Shimadzu, Japan).

2.4. Degradation of methylene blue

Methylene blue, a common dye in the textile industry, was chosen as a typical organic waste. A taper flask (capacity ca. 250 mL) was used as the reactor vessel. The samples (60–100 mg) were added to the system containing methylene blue ($C_{16}H_{18}ClN_3S$) solution (20 mg L^{-1}) 100 mL under stirring. UV–vis absorption spectra were recorded at different intervals to monitor the process. The pH values of the systems were adjusted with dilute HCl solution. In neutral solution, except for methylene blue solution, the system also contained 15 mL of 30 wt% H_2O_2 solution.

3. Results and discussion

3.1. Phase structure

Fig. 1(a) shows the XRD patterns of MnO_2-modified fiberglass composites and MnO_2 nanosheets. The broad diffraction peaks around 25°, which is in line with the pattern of unmodified fiberglass (See Supplementary information, SI-1(a)), indicating amorphous nature of SiO_2 in the fiberglass [19,20]. However, there is extremely weak diffraction peak only at about 12.4° for MnO_2. The diffraction intensities of MnO_2 are so weak and all overlapped or covered by the strong diffraction of the fiberglass (SiO_2), indicating a lower content in weight [21,22]. But the XRD result of MnO_2 nanosheets (collected by removing surface coating from fiberglass composites) exhibits that the diffraction peaks at about 12.3°, 24.5° and 36.7° are almost in accord with the standard XRD pattern of birnessite-type manganese oxide crystal (JCPDS 86-0666), demonstrating δ-MnO_2 exists in the composites.

FT-IR spectrum of MnO_2 nanosheets (Fig. 1b) presents that the broad band around 3440 cm^{-1} represented the O–H antisymmetric stretching vibration of the interlayer water molecules and framework hydroxyl groups, while the band at 1635 cm^{-1} is due to the bending vibrations of O–H groups of the adsorbed water molecules. The sharp absorption peak at 1119 cm^{-1} is assigned to the coordination of Mn by the O–H, and the peaks at 507 and 493 cm^{-1} are considered as the main characteristic absorption bands of birnessite MnO_2, corresponding to Mn–O stretching modes of the octahedral layers in the birnessite structure [23], which are consistent with the previous XRD results. There are no observed absorption bands for birnessite MnO_2 in the composites (SI-1(b)). In addition, the peaks at 1120 and 874 cm^{-1} could be assigned to Si–O symmetric stretching vibration [24,25].

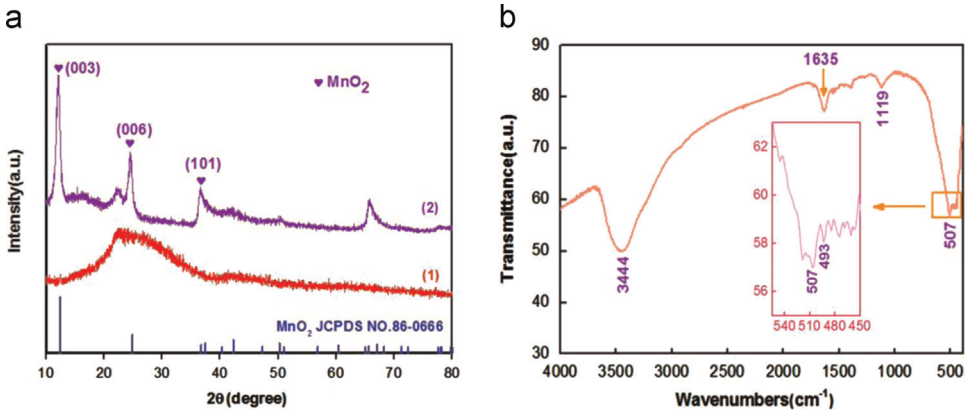

Fig. 1. XRD patterns of (a) MnO_2-modified fiberglass composites and MnO_2 nanosheets, FT-IR spectra of (b) MnO_2 nanosheets. The inset shows enlarged FT-IR spectra of the MnO_2 nanosheets in the range 555–450 cm^{-1}.