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High-yield preparation of K-birnessite layered nanoflake

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ABSTRACT

A high-yield and facile approach for producing K-birnessite layered nanoflake was proposed via simply mixing and hydrothermally heating the mixture of potassium oxalate and potassium permanganate aqueous solution. The product yield was proved to be significantly increased with the addition of potassium oxalate, and the possible reason was also discussed. The product was confirmed to be K-birnessite by a series of characterizations, and fabricated on nickel foam to study the electrochemical behaviors as active electrode material for supercapacitor. Electrochemical results showed that the product exhibited well-performed charge storage properties, and could be promising for applications in energy storage devices.

1. Introduction

In recent years, the society has encountered serious problems like environmental pollution and energy crisis, resulting in the increasing demands for energy storage and conversion. Supercapacitor, as an outstanding alternative of energy storage devices, has been attracting enormous attention due to the long cycle life, fast recharging ability, and high power density [1–4]. Thus, supercapacitors have been applied in a wide range of areas like public transportation, military devices, consumer electronics, and hybrid electric vehicles [5–8]. In order to remarkably improve their performance to meet the future demands, a great many studies have been focused on developing novel supercapacitor electrode materials. To date, a number of materials such as carbons, conductive polymers and transition metal oxides have been considered as excellent candidates as active electrode materials for supercapacitors [9–11]. Comparing with carbons and conductive polymers, transition metal oxides have been extensively employed as potential candidate for the active electrode materials of supercapacitors with excellent performance due to the easy availability, variable oxidation states and good stability during the faradaic reaction [12–14]. Since the electrochemical characteristics of certain transition metal oxides are analogous to that of a battery-type material, which is an important part of hybrid supercapacitor, numerous efforts have been dedicated to develop battery-type materials [15,16]. Among these candidates, manganese oxides are gaining a great much attention owing to the large theoretical capacity, natural abundance, low cost, and environmental friendliness [17]. It has been found that the electrochemical behaviors of manganese oxide materials is strongly influenced by the structure, morphology, pore size and pore volume distributions [18,19]. Accordingly, tremendous efforts have been devoted into the exploration of diverse types of manganese oxide nanomaterials with various morphologies, such as nanospheres, nanowires, nanorods, and nanosheet, and so forth [20–23]. Considering a smaller specific capacity could probably be acquired owing the poor electronic conductivity of a thicker manganese oxide layer [24], birnessite-type might be beneficial in application as active electrode material for supercapacitors taking the advantage of flake-like structure. Combining further investigation on energy storage mechanism, birnessite-type manganese oxides are receiving noticeable interest in this field [25–27]. K-birnessite, as one typical species of birnessite-type manganese oxides, possesses flake-like structure stabilized by K^+ and crystallized water, which should be beneficial to promote the cations' insertion/desertion process [28]. Wet-chemical approach has been well developed for the preparation of K-birnessite nanomaterial, in which pyrolysis of potassium permanganate has been applied for preparing

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K-birnessite nanomaterials in previous reports [29–31]. However, in our preliminary investigation, the production yield of the preparation of K-birnessite employing potassium permanganate as the only raw material was found to be less than 20%, leading to an inefficiency in the fabrication.

In this paper, K-birnessite layered nanoflake was prepared via a hydrothermal approach simply involving potassium permanganate and potassium oxalate as raw materials. The product yield was greatly improved comparing with the product obtained from heating potassium permanganate alone. Electrochemical performances including specific capacity, rate capability and cycling behavior were found to be notable on the K-birnessite nanomaterial as active electrode material, which might promote the applications in energy storage devices.

2. Experimental section

2.1. Materials

All chemicals were of analytical grade and used as received without purification. Water used throughout the whole experiment was ultrapure water with resistivity no less than 18.2 MΩ·cm.

2.2. Synthesis of K-birnessite nanoflake

K-birnessite nanoflake was simply prepared by a hydrothermal route. In a typical procedure, potassium oxalate ($K_2C_2O_4$, 0.37 g) and potassium permanganate ($KMnO_4$, 0.63 g) were mixed in

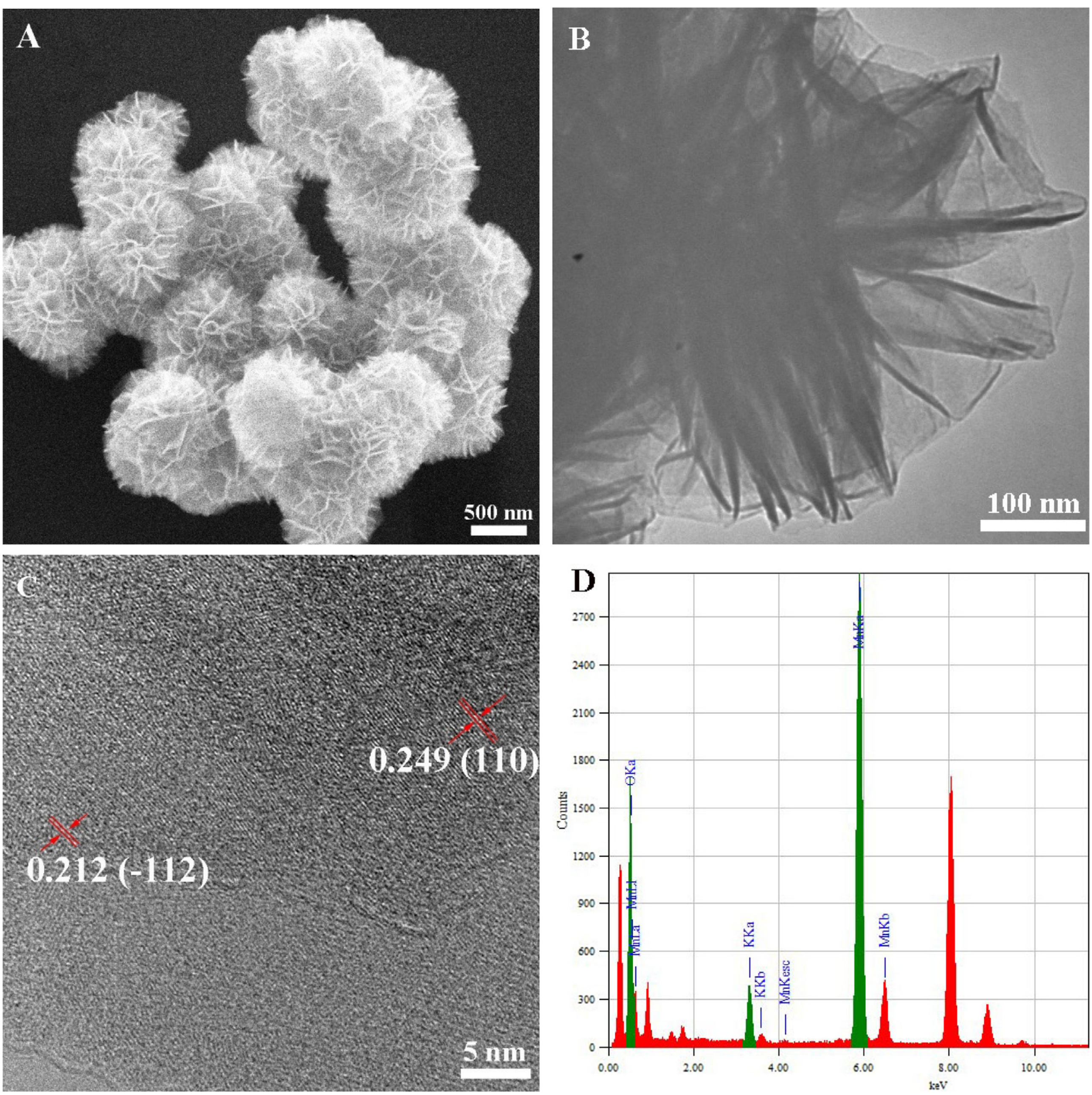

Fig. 1. SEM (A), HRTEM (B, C), and EDX (D) images of the as-prepared KMn48.