Materials Letters 178 (2016) 44–47

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Bismuth oxychloride ultrathin nanoplates as an anode material for sodium-ion batteries

Yan Zhang [a], Shiyu Lu [a], Min-Qiang Wang [a], Yubin Niu [a], Sangui Liu [a], Yutao Li [b], Xiaoshuai Wu [a], Shu-Juan Bao [a], Maowen Xu [a,*]

[a] Institute for Clean Energy & Advanced Materials, Faculty of Materials and Energy, Southwest University, Chongqing 400715, PR China
[b] Texas Materials Institute, University of Texas at Austin, Texas 78712, USA

ARTICLE INFO

Article history:
Received 23 March 2016
Received in revised form
22 April 2016
Accepted 25 April 2016
Available online 26 April 2016

Keywords:
Bismuth oxychloride
Functional
Energy storage and conversion
Sodium-ion battery

ABSTRACT

Two-dimensional bismuth oxychloride (BiOCl) ultrathin nanoplates with a thickness of 10–20 nm are synthesized by a simple hydrothermal method. The as-prepared product is explored as an anode material for sodium-ion batteries for the first time. It shows BiOCl ultrathin nanoplates with two very suitable discharge voltage plateaus (0.6 V and 0.4 V) for sodium ion batteries. Furthermore, a two-step sodiation mechanism including an intercalation reaction and a conversion reaction is proposed. This work reveals a novel electrode material for sodium-ion batteries beyond conventional materials (such as transition metal oxides, carbon materials and alloys) and encourages more researchers to further investigate BiOCl.

1. Introduction

At present, sodium-ion batteries (SIBs) are generally regarded as the most promising alternative for lithium-ion batteries (LIBs) in energy conversion and storage field, and have been widely investigated in the past few years [1]. This is because that the cost of sodium salts is much lower than that of lithium due to its wide distribution and unlimited availability. For SIBs, most research focus on the development of excellent electrode materials [2]. Some cathode materials have been extensively investigated, but anode materials are more challenging [3]. Good performance of hard carbon [4] as an anode material of SIBs was found, but the potential of Na^+ intercalation into hard carbon was very close to that of the metal itself probably causing the formation of dendrites and safe problems. Some low-potential transition-metal oxides also were investigated as anode materials for SIBs. $Na_2Ti_3O_7$ displays a desirable low potential (0.3 V) with the insertion of two additional Na^+ (180 mA h g^{-1}) [5], however, slow rate (C/25) and more addition of carbon black are essential to obtain above capacitance. Tin (Sn) [6] and amorphous phosphorus (P) [7] offer a remarkable capacity, but the large volume expansion effects their cycle performances. Hence, exploration of novel anode materials for SIBs is still a developing process.

MOCl (M=Bi, V et al.) is a series novel layered compounds. BiOCl is widely used in photocatalytic field due to its excellent activity and chemical stability [8]. Recently, VOCl has been reported as cathode material for SIBs [9]. Inspired by above works, we synthesized BiOCl ultrathin nanosheets with a thickness of 10–20 nm by a simple hydrothermal method, and used it as an anode material for SIBs for the first time. The BiOCl samples deliver a high initial discharge capacity of 1050 mA h g^{-1} at two suitable discharge voltage plateaus (0.6 V and 0.4 V).

2. Experimental

The BiOCl nanosheets samples were synthesized by a facile hydrothermal route. Typically, 0.2417 g (0.5 mmol) $Bi(NO_3)_3 \cdot 5H_2O$ and 0.1707 g 2-methylimidazole was dissolved in 20 mL N, N-dimethylformamide (DMF) and 20 mL deionized water, respectively. Then 1 mL HCl (1 M) was added to the $Bi(NO_3)_3$ solution. Afterwards, the 20 mL 2-methylimidazole aqueous solution was also added to the $Bi(NO_3)_3$ solution, resulting in the appearance of white suspension. Then the reaction was carried out in a 40 mL Teflon-lined stainless steel autoclave at 120 °C for 12 h, and finally cooling down to room temperature. The white precipitates were collected by filtration, washed with deionized water several times, and dried at 120 °C under vacuum for 12 h.

Crystallographic phases of the product were investigated by means of powder X-ray diffraction (PXRD) with Cu Kα radiation (λ=1.5416 Å). The morphologies and structures of the resultant samples were observed by using a field-emission scanning electron

* Corresponding author.
E-mail address: xumaowen@swu.edu.cn (M. Xu).

http://dx.doi.org/10.1016/j.matlet.2016.04.197
0167-577X/

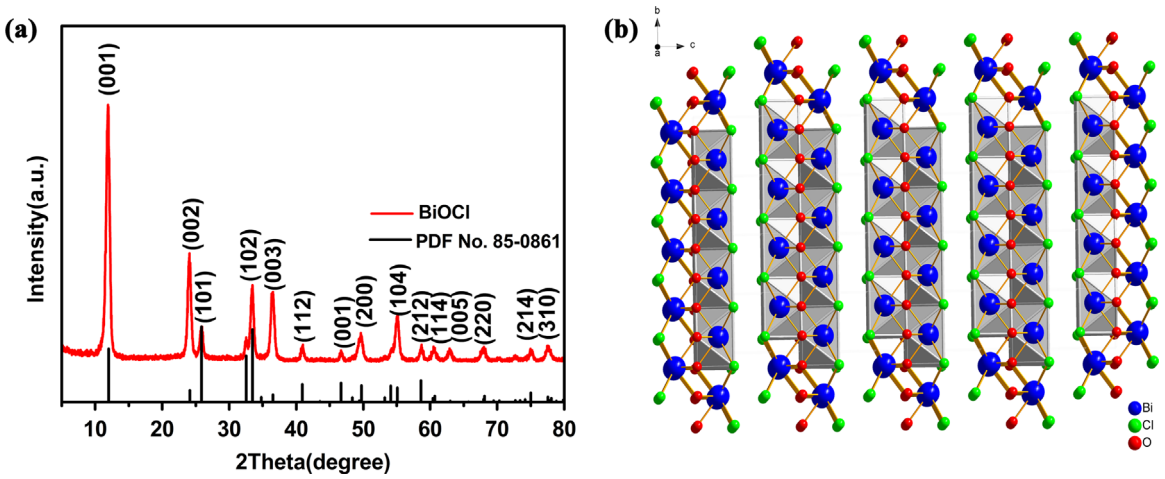

Fig. 1. (a) The PXRD pattern of the as-prepared BiOCl; (b) a schematic illustration of the crystal structure of BiOCl alone the a axis.

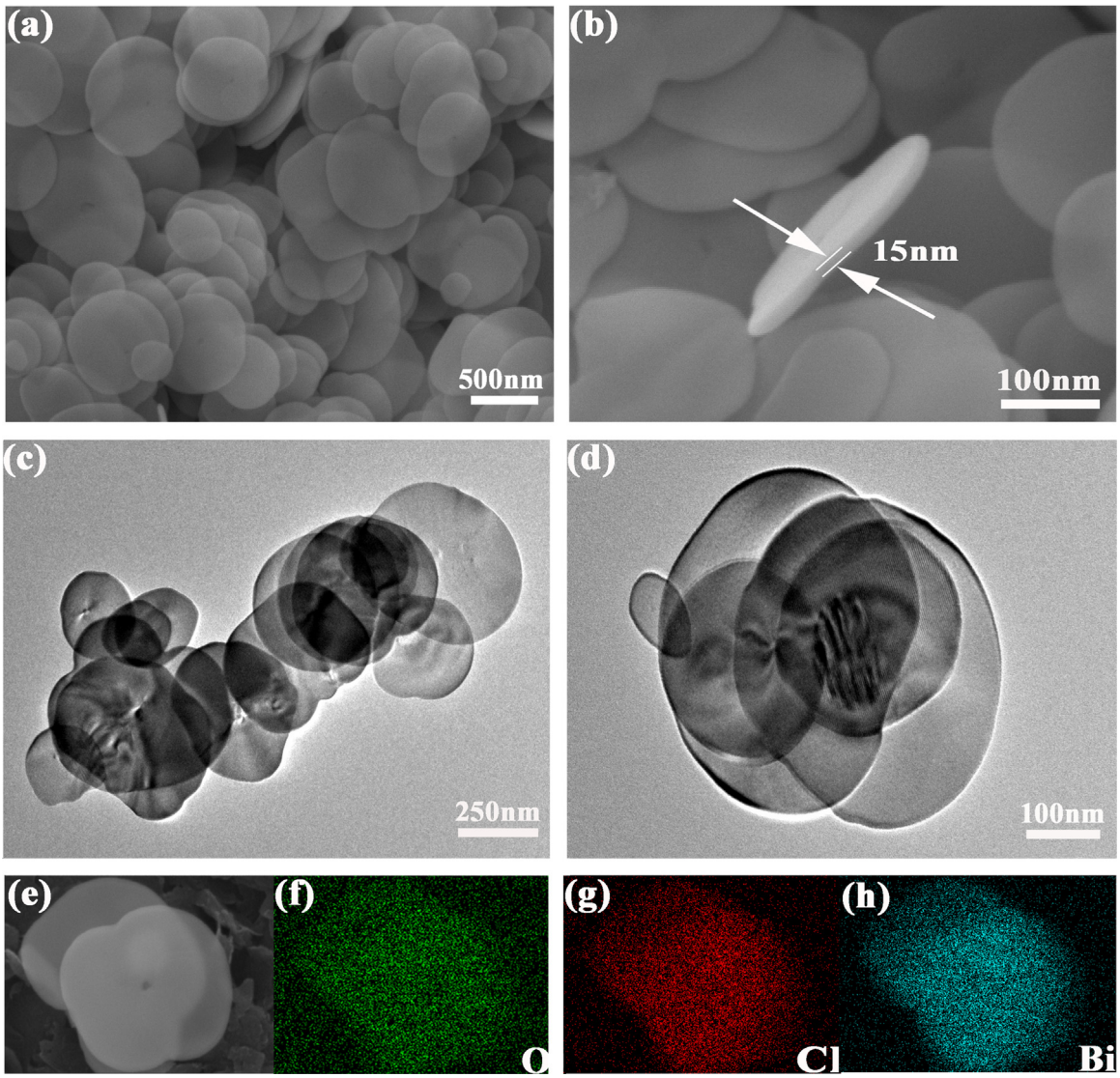

Fig. 2. (a) and (b) FESEM images; (c) and (d) TEM images; (e)–(h) EDS element mapping of the BiOCl samples.

microscope (FESEM) and energy dispersive spectroscopy (EDS; JEOL-6300F), transmission electron microscope (TEM; JEOL-2100 system). For electrochemical tests, the anode materials were evaluated in 2032-type coin cells using a Na disk as counter electrode and 1 M $NaClO_4$ in ethylene carbonate-diethyl carbonate (EC-DEC, 50: 50 vol%) solution as electrolytes. The composite anode was prepared by mixing active material (BiOCl), super-P carbon black, and carboxymethyl cellulose (CMC) binder in the weight ratio of