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Short communication

A self-supported metal-organic framework derived Co_3O_4 film prepared by an *in-situ* electrochemically assistant process as Li ion battery anodes

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HIGHLIGHTS

- Co-ZIF67 MOFs were synthesized by an electrochemical method on Ti nanowire arrays.
- Co_3O_4 blocks derived from the MOFs were anchored by Ti nanowire arrays.
- The Co_3O_4/Ti was used as self-supported anodes of Li ion batteries.
- Good conductivity and adherence lead to remarkable rate capability and durability.

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ABSTRACT

Derivates of metal-organic frameworks are promising materials of self-supported Li ion battery anodes due to the good dispersion of active materials, conductive scaffold, and mass transport channels in them. However, the discontinuous growth and poor adherence of metal-organic framework films on substrates hamper their development in self-supported electrodes. In the present study, cobalt-based metal-organic frameworks are anchored on Ti nanowire arrays through an electrochemically assistant method, and then the metal-organic framework films are pyrolyzed to carbon-containing, porous, self-supported anodes of Li ion battery anodes. Scanning electron microscope images indicate that, a layer cobaltosic oxide polyhedrons inserted by the nanowires are obtained with the controllable *in-situ* synthesis. Thanks to the good dispersion and adherence of cobaltosic oxide polyhedrons on Ti substrates, the self-supported anodes exhibit remarkable rate capability and durability. They possess a capacity of 300 mAh g^{-1} at a rate current of 20 A g^{-1}, and maintain 2000 charge/discharge cycles without obvious decay.

1. Introduction

Derivates of metal-organic frameworks (MOFs) have tremendous potential as electrode materials of electrochemical energy storage and transformation devices owing to their abundant active sites, sufficient channels, and good conductivity [1–4]. In diverse applications, pyrolyzing MOFs to transition metal oxides (TMOs) then using them as lithium ion battery (LIB) anode materials has drawn considerable attention [5–10]. Small grain size of TMOs and sufficient pores in the materials enable the LIB anodes accommodating the volume change effectively in Li^+ insertion/extraction [11–17]. The channels and carbon scaffolds derived from MOF precursors lead to facilitated ion and electron transport in charge/discharge [18–21]. These features are beneficial to capacity, rate capability and durability of LIB anodes. Furthermore, the unique configuration enables MOF derivates to be good candidates of self-supported anodes that free of conductive agents and binders. In contrast to conventional anodes obtained from rolling paste, self-supported anodes possess exceeding capacity density and rate capability due to more rational design [22–27]. The MOF derivates exactly cater to the design requirement of additive- and binder-free anodes by embedding conductive scaffolds and mass transport channels into the active materials. Unfortunately, the limited size of MOF blocks causes their reluctant growth in a continuous large-area form. Generally, they prefer growing to dispersive and small particles, and this results in preparing self-supported continues MOF films is rare, especially on a porous conductive substrate. Additionally, dissatisfactory adherence of MOFs with substrates further causes that, preparing self-supported anodes by directly pasting them on current collectors is

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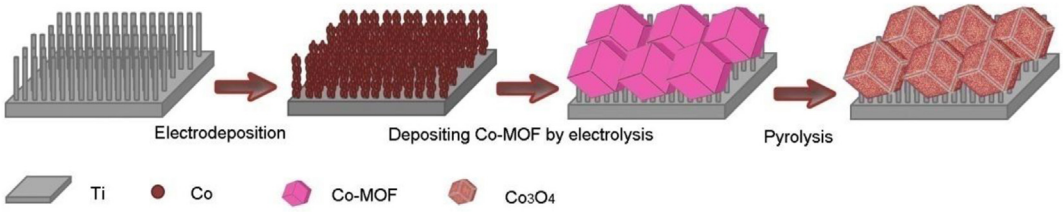

Fig. 1. Schematic diagram of preparing Co-MOF derived Co_3O_4 on Ti nanowire arrays.

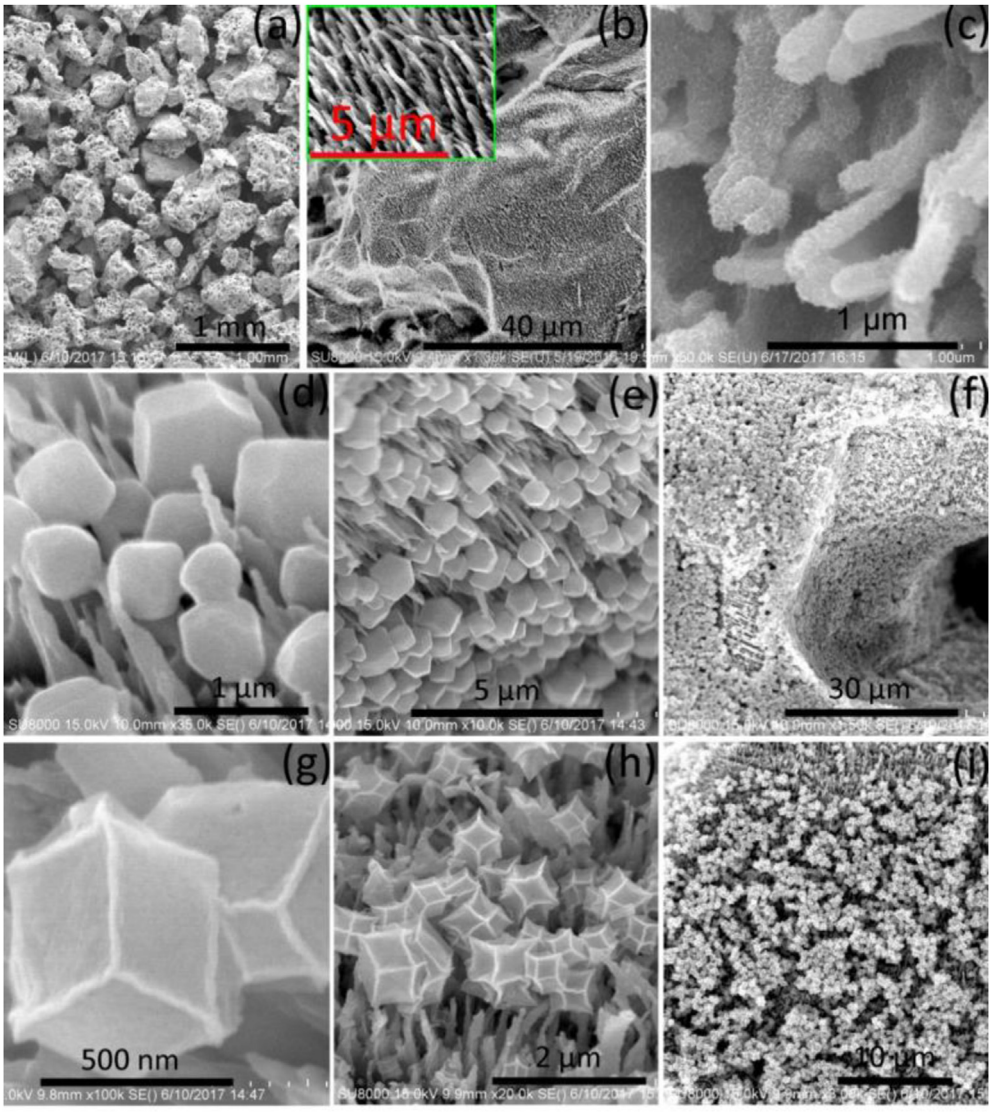

Fig. 2. SEM images of Ti foam (a), Ti nanowire arrays (b), Co coated Ti nanowires (c), Co-MOFs on Ti nanowire arrays (d, e, f), and Co_3O_4 derived from Co-MOFs on Ti nanowire arrays (g, h, i). The inset in (b) is the magnified images of Ti nanowires.

difficult [28–30]. Electrochemical synthesis is a suitable method to settle these issues because of its good controllability and the *in-situ* growth of MOFs in electrochemical processes [31].

In the present study, we used vertically standing Ti nanowire arrays as substrates for preparing Co-ZIFs by an *in-situ* electrochemically assistant method. The *in-situ* electrochemical process generated the architecture of Ti nanowires inserting into MOF blocks, and this guaranteed good adherence of MOF films on the substrates. Furthermore, the Ti nanowires connected with the carbon scaffolds in the blocks after pyrolyzing the MOF precursor, and this enabled good electron transport in the self-supported electrodes. Additionally, the good controllability of electrochemical synthesis afforded help for preparing unilaminar MOFs on the substrates, in which, the MOF blocks exhibited uniform distribution. These advantages leaded to good rate capability and durability of the self-supported anodes. They possessed a capacity of 300 mAh g^{-1} at a rate current of 20 A g^{-1}, and maintained 2000 charge/discharge cycles without obvious decay.

2. Experimental

2.1. Fabrication of Co-MOF membranes on Ti nanowire arrays

All the regents in the present study are analytical reagents. Ti nanowire arrays were fabricated on circular Ti (Ti—Mo alloy, Mo = 0.3 wt