Journal of Alloys and Compounds 685 (2016) 15–21

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Synthesis of porous nickel networks supported metal oxide nanowire arrays as binder-free anode for lithium-ion batteries

Q.Q. Xiong*, H.Y. Qin, H.Z. Chi, Z.G. Ji

College of Materials and Environmental Engineering, Hangzhou Dianzi University, Hangzhou 310018, China

ARTICLE INFO

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

Keywords:
3D nickel network
Composite materials
Lithium-ion batteries
Energy storage and conversion
Cobalt oxides

ABSTRACT

Directional design/preparation of porous metal/metal oxides composite arrays is critical for construction of advanced optical-electrochemical devices. Herein we report three-dimensional (3D) porous Ni networks supported cobalt oxide nanowire arrays (Ni-Co_3O_4 NWs) by combining electro-deposition and hydrothermal process. 3D Ni networks with porous branches and interconnected pores are well formed and used as the skeleton for the growth of cobalt oxide nanowire arrays. High porosity and integrated growth are combined in the composite electrode. Due to the unique composite architecture, the Ni-Co_3O_4 NWs electrode exhibits higher discharge capacities, better cycling stability (714 mAh g^{-1} at 0.5 A g^{-1} after 100 cycles), and enhanced rate capability, as compared to the Ni networks supported dense Co_3O_4 film (Ni-Co_3O_4 dense film). The proposed method is useful for construction of other porous metal/metal oxide composite films for application in electrochemical catalysis, energy storage and sensing.

1. Introduction

Lithium ion batteries (LIBs) are becoming the energy market pet and usually used as the main power source because of their high energy density and high working voltage [1–3]. To further improve the electrochemical performance of LIBs, in parallel with the exploitation of advanced cathode materials, great efforts are devoted to exploring novel anode materials with high capacity. Attractively, cobalt oxide (Co_3O_4) is one of them owing to its high reactivity and high theoretical capacity (~890 mAh g^{-1}) about 2–3 times larger than that of commercial graphite [4,5]. Unfortunately, Co_3O_4 still suffers from some issues: rapid capacity loss associated with large volume changes, and compromised rate capability because of low electrical conductivity. The former will cause pulverization and crushing of the electrode and accelerate the degradation of electrochemical performance. The latter is related to their low intrinsic conductivity, which is not favorable for fast electron transfer resulting in low reaction kinetics [6]. To surpass the shortcomings mentioned above, the common strategy is to synthesize Co_3O_4 nanostructures with short ion diffusion path and increased active surface area, leading to improved utilization of active materials and better cycling stability. In particular, compared with nanoparticles, one-dimensional nanowire/nanorod structures have arouse considerable interest due to their faster Li^+ diffusion, and more accessible electroactive sites [7–9]. In addition, composite nanostructuring with porous conductive matrixes can further provide fast electron transportation path, resulting in faster reaction kinetics and better rate capability [10]. Recently, combining 3D porous metal matrixes and nanostructured metal oxides in one electrode is a fascinating approach and possesses the above merits to construct high-performance anodes [11,12].

Over recent years, 3D porous metal networks prepared using hydrogen bubbles template are becoming a rising area due to their unique structural features and high electrical conductivity [13,14]. Thus, it would be very interesting to combine 1D Co_3O_4 nanowires and 3D porous metal networks in one integrated electrode, and no similar result has been reported. In the present work, we report direct growth of Co_3O_4 nanowire arrays on 3D porous Ni networks as binder-free anode for LIBs. The preliminary electrochemical properties of the Ni-Co_3O_4 NWs have been characterized and higher capacity and better cycling life are demonstrated, as compared to the Ni-Co_3O_4 dense film. This enhancement is mainly benefited from the nanoscale combination between 3D porous Ni networks and Co_3O_4 nanowire arrays. Our electrode design protocol may be useful for fabrication of other metal/metal oxides composite electrodes for supercapacitors and batteries.

* Corresponding author.
E-mail address: zjxqq@hdu.edu.cn (Q.Q. Xiong).

http://dx.doi.org/10.1016/j.jallcom.2016.05.258
0925-8388/

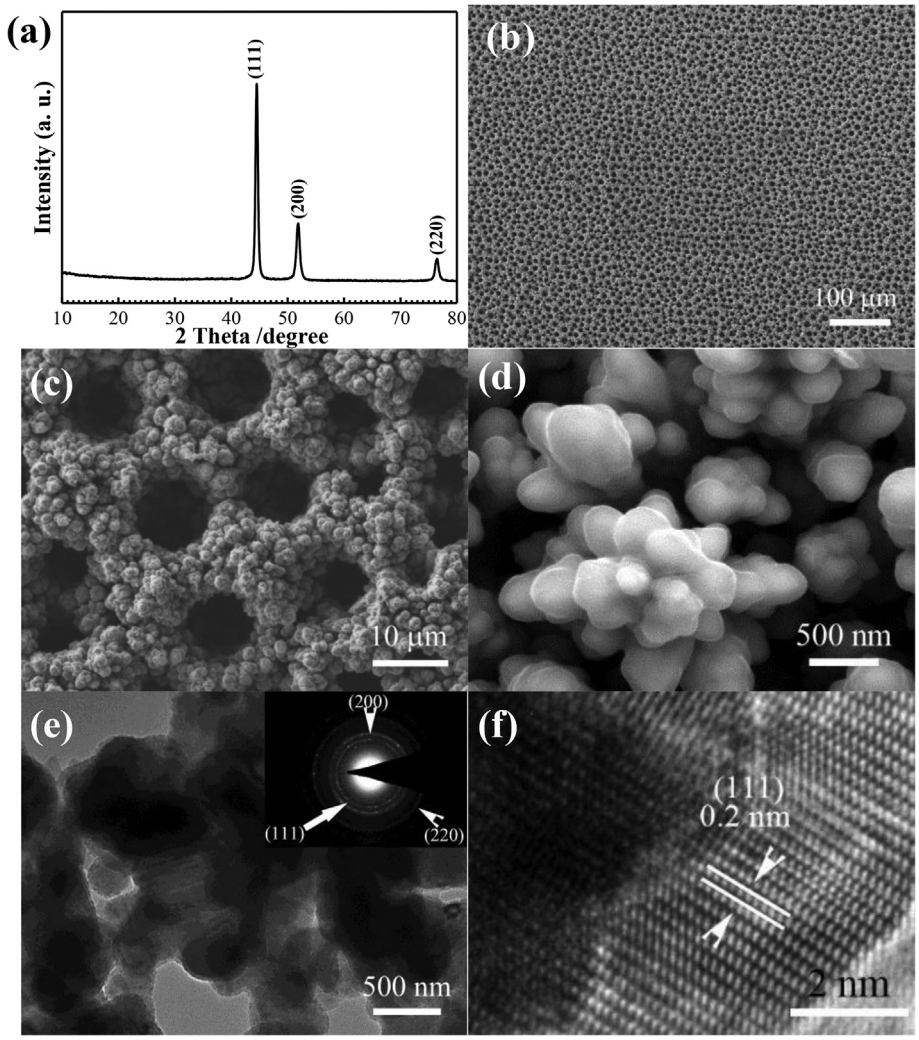

Fig. 1. (a) XRD pattern of the 3D porous Ni networks scratched from the substrate; (b, c, d) SEM images of 3D porous Ni networks with low and high magnification, respectively; (e, f) TEM images of 3D porous Ni networks with low and high magnification (SAED pattern in inset).

2. Experimental

The 3D porous nickel networks supported Co_3O_4 nanowire arrays were fabricated as follows. First, 3D Ni networks were

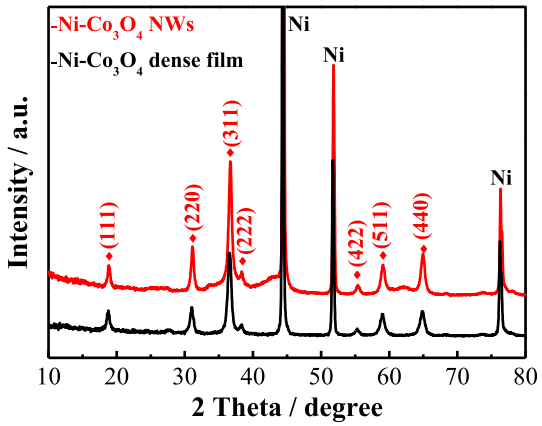

Fig. 2. XRD patterns of the Ni-Co_3O_4 NWs and Ni-Co_3O_4 dense film scratched from the substrate.

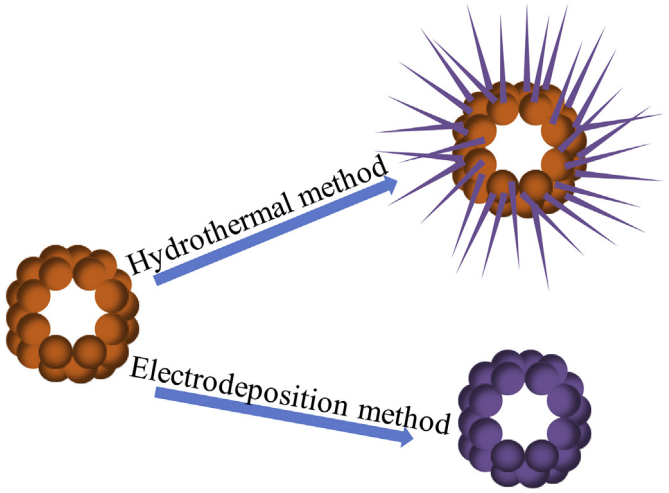

Fig. 3. A schematic illustration of the formation of the Ni-Co_3O_4 NWs and Ni-Co_3O_4 dense film.