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Cobalt oxide modified porous carbon anode enhancing electrochemical performance for Li-ion batteries

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ABSTRACT

A cobalt oxide modified porous carbon has been synthesized via a solvothermal method followed by a simple thermal treatment process. Scanning electron microscopy and transmission electron microscopy images reveal that Co_3O_4 nanoparticles (NPs) with sizes of 20–40 nm are uniformly anchored onto porous carbon (PC). As an anode material for Li-ion batteries (LIBs), the composite exhibits enhanced reversible capacity, excellent cyclic performance, high Coulombic efficiency and good rate capability, which could be attributed to the 3D hierarchical porous structure of PC as well as the small size of the Co_3O_4 NPs providing convenient and accessible routs for electrolyte diffusion and intercalation of Li ions. Moreover, the interconnective networks of PC could decrease the inner resistance of LIBs and maintain structural stability. Thus the Co_3O_4/PC composite could be a promising anode material for high-performance LIBs.

1. Introduction

With increasing demand in electric energy storage for electric vehicles and modern electronics, high-performance Li-ion batteries (LIBs) have attracted extensive research interest due to their fascinating advantages such as high energy density, long cycle life, low self-discharge, high operating voltage and excellent rate performance [1–4]. Graphitic carbons have been predominantly employed as the anode materials in commercial rechargeable LIBs originating from their low cost, low toxicity, good conductivity and chemical stability, in addition to a desirable electrochemical profile. However, because of the low theoretical specific capacity (372 mAh g^{-1}) of graphite, they could hardly satisfy the growing demand of energy storage system, and provide ample opportunities for exploring alternative high-performance anode materials [5–7].

In term of high specific capacity, nanostructured transition metal oxides have been considered to be promising anode materials in LIBs [8–14]. Among them, Co_3O_4 was reported to show a high theoretic reversible specific capacity of 890 mAh g^{-1} about more than two times higher than those of graphite anodes. But its intrinsic low electrical conductivity, large volume change and severe particle aggregation, which occur during charge/discharge processes, result in a large irreversible capacity loss and poor cycling stability. In order to overcome aforementioned problems, hybridizing Co_3O_4 nanoparticles (NPs) with conducting matrices having different morphological structures has been demonstrated one of the most potentially effective approaches [15–20].

Recently, hierarchical porous carbons (HPCs) were proposed to be an advanced anode material in LIBs due to the expected reduced diffusion length of Li ions and rapid charge transfer [21,22]. More importantly, HPCs in composites with metallic or oxide nanoparticles can provide a support for anchoring well-dispersed nanoparticles and function as a highly conductive matrix for enabling good contact between the components. Furthermore, HPCs can effectively alleviate the volume expansion/contraction and aggregation of nanoparticles during the charge/discharge processes. Therefore, it is expected that the composite of electrically conductive HPCs anchored with Co_3O_4 NPs can efficiently utilize the combinative merits of Co_3O_4 and HPCs and shows superior performance as the anode material of LIBs.

Herein, we report the synthesis of a composite of electrically conductive porous carbon anchored with Co_3O_4 NPs (Co_3O_4/PC), which displays enhanced reversible capacity, excellent cyclic performance, high Coulombic efficiency and good rate capability as an anode material for LIBs. It highlights the importance of the

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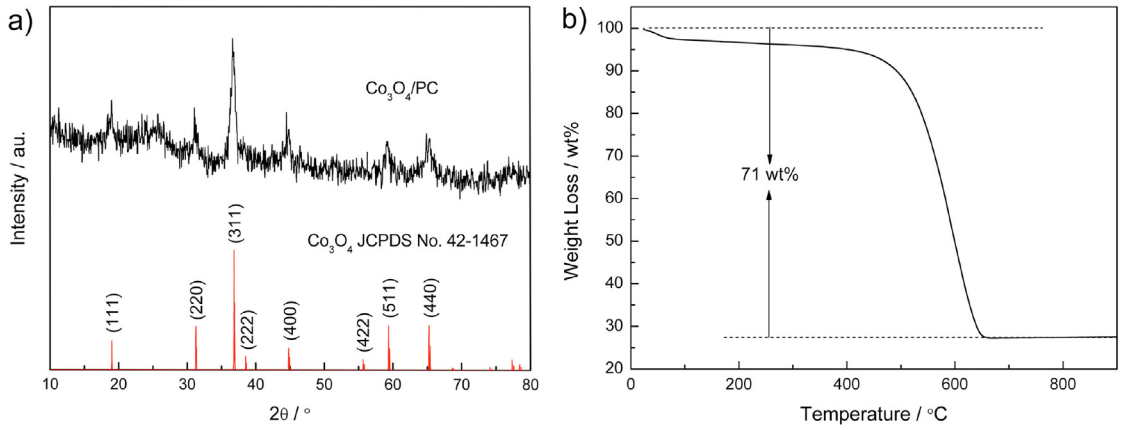

Fig. 1. (a) XRD pattern and (b) TGA curve of the Co3O4/PC composite.

anchoring Co_3O_4 onto PC for maximum utilization of electrochemically active Co_3O_4 and PC for energy storage applications.

2. Experimental

2.1. Materials synthesis and characterization

The synthesis of the cobalt oxide modified porous carbon was based on a simple hydrothermal method using colloidal silica as template. First, the colloidal silica was prepared by Stöber method and surface modified by 3-amino-propyltrimethoxysilane (APMS) as reported previously [23,24]. Then, 0.2 g glucose, 0.028 g $CoSO_4{\cdot}7H_2O$ and 0.012 g $CO(NH_2)_2$ were dissolved in the obtained silica colloid (20 ml) under stirring. After stirring for 30 min, the obtained homogeneous solution was transferred and sealed in an 25 mL Teflon-lined autoclave, and maintained at 180 °C for 24 h. The solid product was obtained by centrifugation, wash and dried at 100 °C for 12 h. Finally, the as-prepared composite was carbonized at 800 °C for 2 h at N_2 flowing and followed by 2 M NaOH etching to remove silica. The cobalt oxide modified porous carbon (Co_3O_4/PC cmposite) was obtained. For comparison, honeycomb hierarchical porous carbon (PC) with a similar structure was prepared according our reported method [24]. The pure Co_3O_4 was synthesized by thermal decomposition of commercial $CoCO_3$ under air.

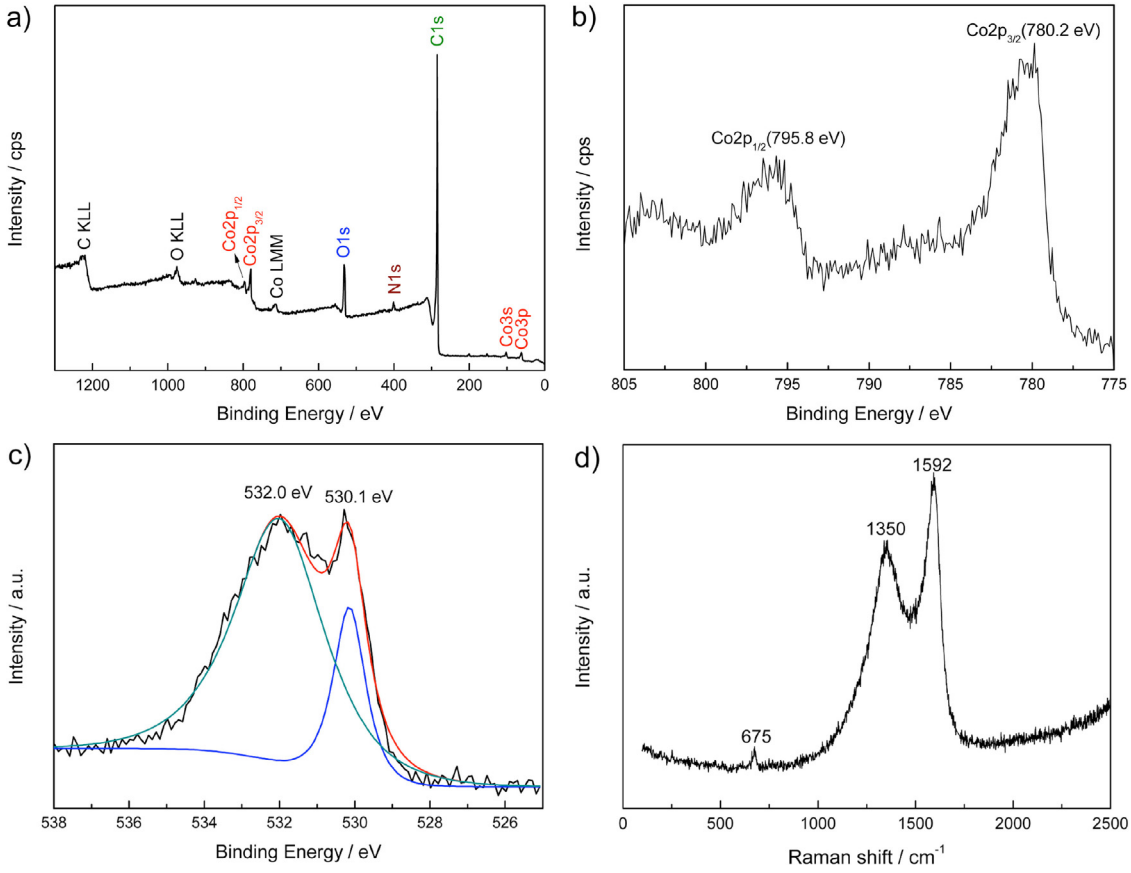

Fig. 2. XPS spectra of the survey scan (a), Co 2p (b) and O 1 s (c) region of the Co_3O_4/PC composite. (d) Raman spectrum of the Co_3O_4/PC composite.