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Cobalt oxide hollow microspheres with micro- and nano-scale composite structure: Fabrication and electrochemical performance

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ABSTRACT

Co_3O_4 hollow microspheres with micro- and nano-scale composite structure self-assembled by nanosheets were successfully fabricated by the template-free wet-chemical approach. This method is simple, facile and effective. The Co_3O_4 hollow microspheres with good purity and homogeneous size were well characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transform IR (FTIR), thermogravimetric analysis (TGA) and inductively coupled plasma atomic emission spectrometer (ICP). The formation mechanism was deeply studied. The micro- and nano-scale composite structure constructed by the porous nanosheets promotes to improve the electrochemical properties of Co_3O_4 hollow microspheres. The high discharge capacity of 1048 mAh g^{-1} indicates it to be the potential application in electrode materials of Li-ion battery.

1. Introduction

In the past 15 years or so, various synthesis methods for a wide range of nanoparticles with different shapes were established [1–6]. In recent years, many efforts have been focused on assembling one-dimensional (1-D) nanoscale building blocks into two- and three-dimensional (2-D and 3-D) ordered superstructures or complex functional architectures, which is a crucial step toward the realization of functional nano-devices [7]. However, in addition to common 1-, 2-, and 3-D architectures, controlled organization of primary building units into curved structures represents another challenge for exploiting new functional materials, because hollow structures are highly demanded in new technological applications [8–12].

Spinel Co_3O_4 is an important functional material for a wide range of technological applications such as heterogeneous catalysts, anode materials in Li-ion rechargeable batteries, solid-state sensors, magnetism, and optical devices [13–23]. Owing to the influence of particle size and morphology on the properties of materials, the controlled preparation of Co_3O_4 particles of different sizes and morphologies is always the researcher's purpose. Up to now, Co_3O_4 particles with various morphologies, such as nanotubes [13], nanorods [13], nanosheets [14], hollow nanospheres [15] and nanocubes [16], have been prepared. However, few literatures have been reported on micro- and nano-scale composite Co_3O_4 hollow microspheres with high purity and homogeneous size.

In this paper, we describe a facile template-free wet-chemical approach [24,25] to fabricating Co_3O_4 hollow microspheres with micro- and nano-scale composite structure self-assembled by nanosheets. In the reaction system, cobalt chloride is used as cobalt source and ethylene glycol (EG) as solvent. The hollow spherical intermediate complex (Co–EG coordination polymer) was obtained first by the wet-chemical method. After annealing at 500 °C for 20 min under air, Co_3O_4 hollow microspheres with the similar morphology were formed (see experimental section for the details). Electrochemical results indicate that Co_3O_4 hollow microspheres as the electrode material of Li-ion battery have the high discharge capacity of 1048 mAh g^{-1}.

2. Experimental section

$CoCl_2 \cdot 6H_2O$ (0.7138 g, 3 mmol) was dissolved in EG (24 mL) to form a transparent solution, and then sodium acetate (CH_3COONa, NaAc) (2.16 g) and polyethylene glycol 200 (PEG200) (0.6 g) were added into the above solution. The mixed solution was stirred and gradually became transparent, and then sealed in a Teflon-lined stainless-steel autoclave (30 mL capacity). The autoclave was heated to and maintained at 180 °C for 12 h, and allowed to cool to

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room temperature. The peach products were collected and rinsed more than five times by ethanol, and dried at 60 °C for 5 h, which was the intermediate complex of Co_3O_4 hollow microspheres. After the peach product was annealed at 500 °C for 20 min, Co_3O_4 hollow microspheres were obtained.

The as-prepared samples were characterized by transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and fast Fourier transform (FFT) (Fecnai G^2 20 S-TWIN from FEI Corporation, 200 kV), energy dispersive X-ray (EDX, GENESIS2000 XMS from EDAX corp. 200 kV), scanning electron microscopy (SEM, JEOL JSM-5610 LV SEM, 20 kV), X-ray diffraction (XRD, D/Max-RA diffractometer, Cu$K\alpha$ radiation), Fourier transform IR (FTIR, VECTOR 22 from BRUKER), thermogravimetric analysis (TGA, LABSYS from SWTERAM), and inductively coupled plasma atomic emission spectrometer (ICP, JA1100 from Jarrell-Ash Corp.).

Co_3O_4 electrode was prepared by coating an active paste into aluminum foil. A paste contained 80 wt% Co_3O_4, 10 wt% carbon black, and 10 wt% polytetrafluoroethylene (PTFE). The coated electrode was placed in vacuum at 100 °C for at least 8 h. Electrochemical performance was measured on Roofer Battery Tester from ShenZhen, China, under labconco glovebox protected by argon gas in electrochemical cell of two electrodes, which contained the cobalt oxide working electrode and lithium counter

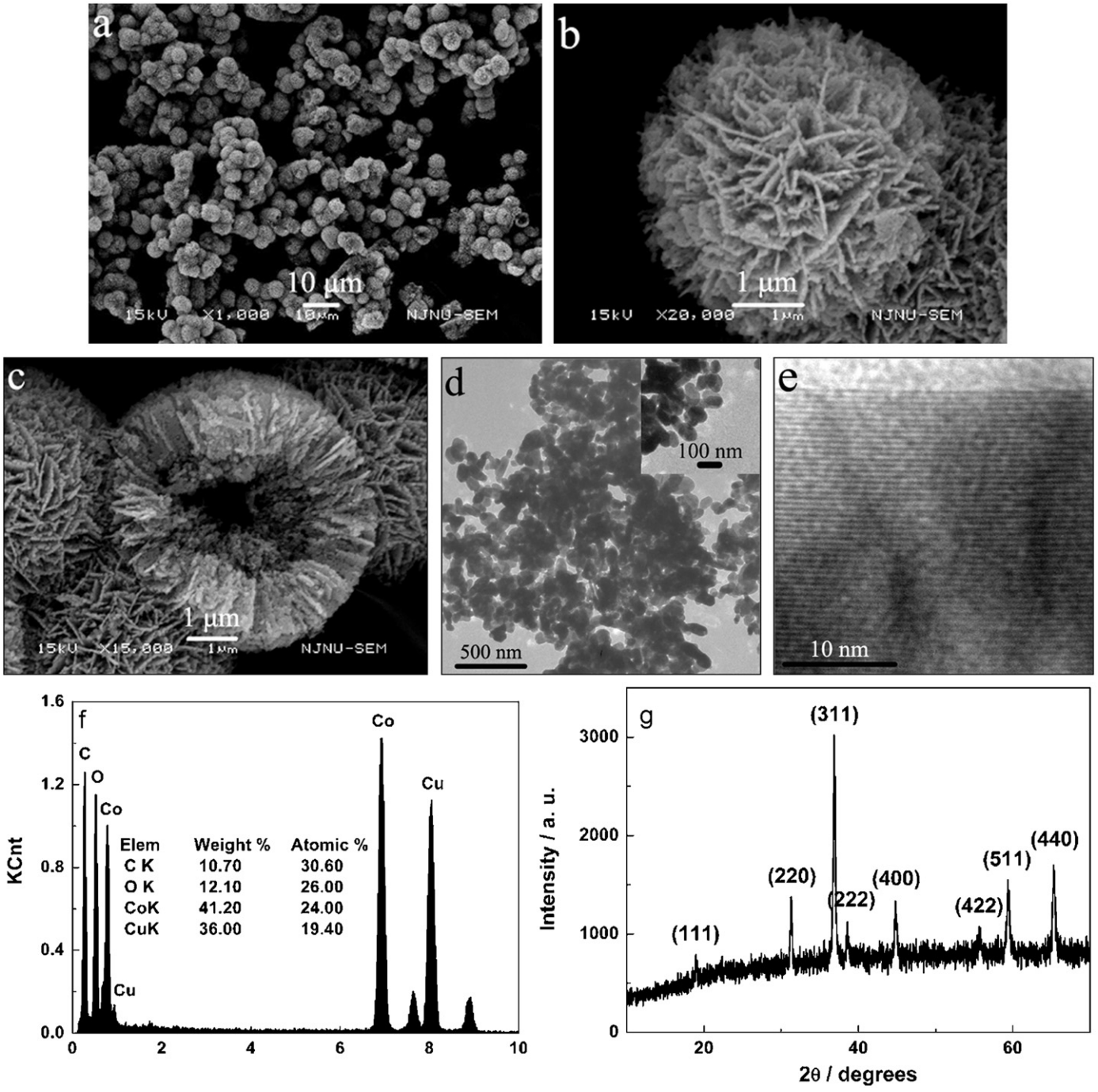

Fig. 1. SEM images (a–c) of Co_3O_4 hollow microspheres: (a) the low magnification, (b) a whole microsphere, and (c) a broken microsphere. TEM (d) and HRTEM images (e) of a nanosheet constructing Co_3O_4 hollow microspheres, and the inset in Fig. 1d shows the TEM image of the verge of a nanosheet. EDX analysis (f) and XRD pattern (g) of Co_3O_4 hollow microspheres.