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Synthesis of Co_2SnO_4@C core–shell nanostructures with reversible lithium storage

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ABSTRACT

This paper reports the synthesis of Co_2SnO_4@C core–shell nanostructures through a simple glucose hydrothermal and subsequent carbonization approach. The as-synthesized Co_2SnO_4@C core–shell nanostructures have been applied as anode materials for lithium-ion batteries, which exhibit improved cyclic performance compared to pure Co_2SnO_4 nanocrystals. The carbon matrix has good volume buffering effect and high electronic conductivity, which may be responsible for the improved cyclic performance.

1. Introduction

Rechargeable lithium-ion batteries are currently the dominant power source for portable electronic devices and considered to be the prime candidate for the next generation of electric vehicles [1]. Graphite is now used as anode materials in most commercial Li-ion batteries. However, the limited gravimetric capacity (372 mAh g^{-1}) of carbon has prompted intensive research for alternative anode materials that have large capacity at low potentials [2]. Since the discovery of 3*d* transition-metal oxides with good performance as the anode materials of Li-ion batteries, a great effort has been made to improve their capacity and cycling performance [3]. Among them, cobalt oxides (Co_3O_4, CoO) demonstrated the best electrochemical properties in Li-ion batteries, compared to nickel oxide and iron oxides [4–6]. Many efforts were made to replace cobalt partially by environment-friendly and less-expensive alternative metals to lower the toxicity and reduce the cost [7–9]. As a result, the ternary cobalt-based metal compounds such as Co_2SnO_4 have been realized as anode materials of Li-ion batteries [10–12]. In this compound, the oxidation and reduction reactions are involved for cobalt oxides, and lithium alloying exists in the subsequent reaction of the tin oxides. Such multi-electron reactions in the electrochemical processes lead to higher electrochemical capacity. Recently, extensive work has been focused on the synthesis of metal oxide–carbon hybrid nanostructures as anode materials to enhance the lithium storage performance by introducing carbon as "buffering matrixes" [13–20]. Therefore, Co_2SnO_2–C hybrid nanostructures are expected to show the improved electrochemical performance.

Herein, we report the synthesis of Co_2SnO_4@C core–shell nanostructures through a simple glucose hydrothermal and subsequent carbonization approach. The Co_2SnO_4@C core–shell nanostructures with carbon layers of different thickness have been prepared and applied as anode materials for lithium-ion batteries, which exhibit higher lithium storage capacities and better cycling performance compared to pure Co_2SnO_4 nanocrystals.

2. Experimental

2.1. Synthesis of Co_2SnO_4 nanocrystals

All the chemicals were analytical grade without further purification. Co_2SnO_4 nanocrystals were prepared by a hydrothermal route in NaOH solution [12]. Briefly, 4 mmol $CoCl_2{\cdot}6H_2O$ and 2 mmol $SnCl_4{\cdot}5H_2O$ were dissolved into 60 ml distilled water to form a transparent solution. Then 20 ml 1 M NaOH solution was dropped into the Co–Sn mixture solution under magnetic stirring. The final solution was transferred into a 100 ml Teflon-lined stainless steel autoclave, sealed, and maintained at 250 °C for 24 h. After the reaction was finished, the resulting blue solid products were centrifuged, washed with distilled water and ethanol to remove the

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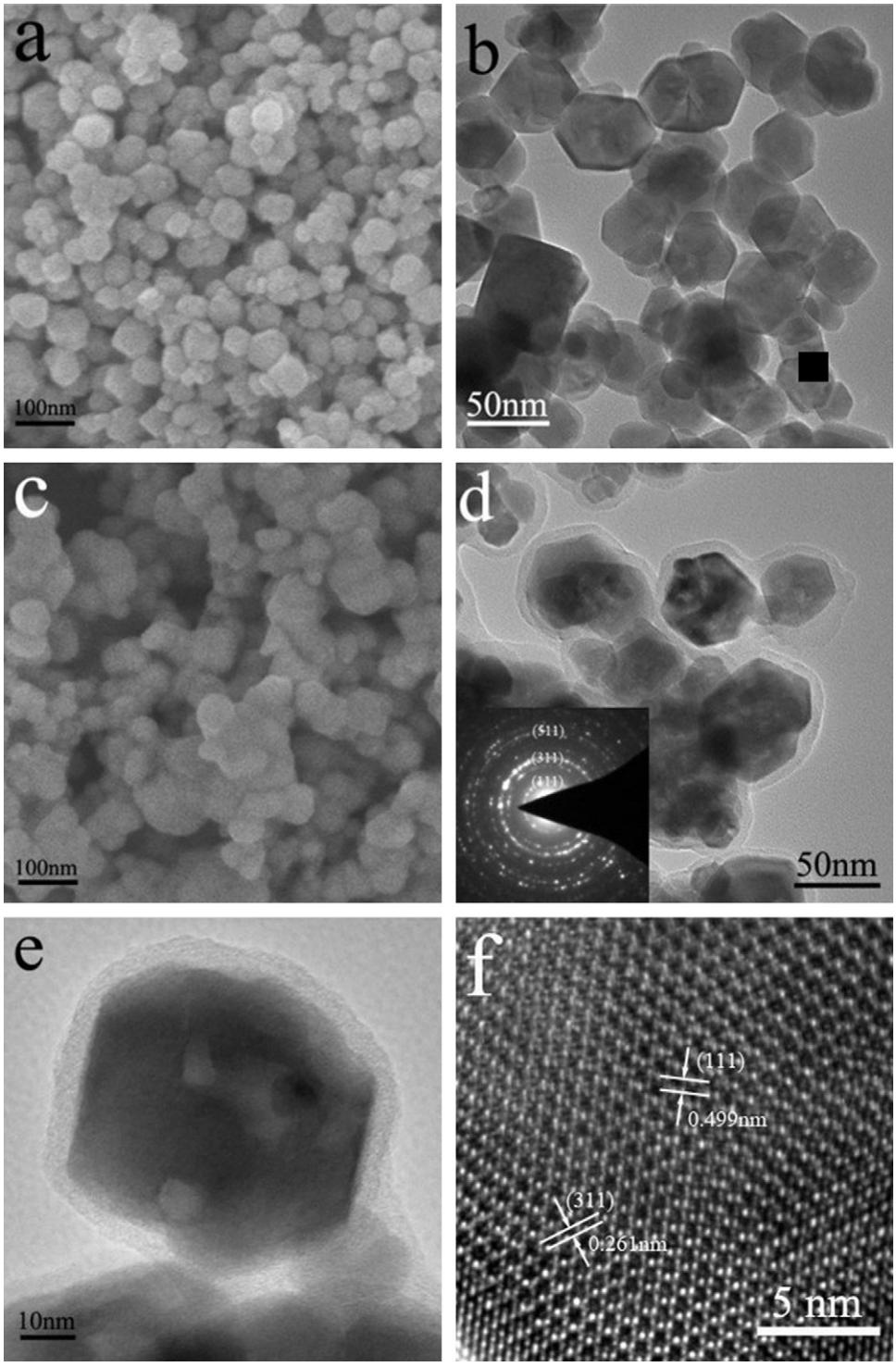

Fig. 1. FESEM image (a) and TEM image (b) of pure Co_2SnO_4 nanocrystals, and morphological and structural characterizations of Co_2SnO_4@C nanostructures: FESEM image (c); TEM image and its SAED pattern (inset) (d); magnified TEM image (e); HRTEM image (f).

ions possibly remaining in the final products, and finally dried at 60 °C in air.

2.2. Synthesis of Co_2SnO_4@C core–shell nanostructures

Co_2SnO_4@C core–shell nanostructures were prepared by a glucose hydrothermal process and subsequent carbonization approach [19,20]. Briefly, 0.4 g Co_2SnO_4 nanocrystals were dispersed in 40 ml 0.25 M aqueous glucose solution. After sonication for 20 min, the solution was transferred into a 50 ml Teflon-lined stainless steel autoclave, sealed, and maintained at 180 °C for 12 h. After the reaction was finished, the resulting solid products were centrifuged, washed with distilled water and ethanol to remove the ions possibly remaining in the final products, and then dried at 80 °C under vacuum. Finally, the products were kept in a tube furnace at 500 °C for 3 h under N_2 at a ramping rate of 5 °C min^{-1}.