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Hollow carbon spheres with encapsulation of Co_3O_4 nanoparticles as anode material for lithium ion batteries

Liang Zhan [a,b,*], Yanli Wang [a], Wenming Qiao [a], Licheng Ling [a], Shubin Yang [b,**]

[a] State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, PR China
[b] Mechanical Engineering and Material Science, Rice University, Houston 77005, USA

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ABSTRACT

Based on the high theoretical capacity of Co_3O_4 for lithium storage, a noval type of monodisperse hollow carbon spheres with encapsulation of Co_3O_4 nanoparticles (HCSE-Co_3O_4) were designed and synthesized. The monodisperse hollow carbon spheres not only can provide enough void volume to accommodate the volume change of encapsulated Co_3O_4 nanoparicles, but also can prevent the formation of solid electrolyte interface (SEI) films on the surface of Co_3O_4 nanoparticles and following direct contact of Co and SEI films upon lithium extraction. The HCSE-Co_3O_4 electrode exhibit highly reversible capacity, excellent cycle performance and rate capability attributed to the unique structure. The reversible capacity of HCSE-Co_3O_4 electrode is as high as 500 mAh g^{-1} at a current density of 744 mA g^{-1}, while that of bare Co_3O_4 electrode is only around 80 mAh g^{-1}.

1. Introduction

Lithium ion batteries, as power sources for portable electronic devices and electric/hybrid vehicles, have attracted tremendous attentions in the scientific and industrial fields due to their high electromotive force and high energy density. To meet the increasing demand of batteries with higher energy density and longer cycle life, many efforts have been made recently to develop new electrode materials or design novel structures of electrode materials [1–8]. For anode materials, transition-metal oxides such as Co_3O_4 [9–11], Fe_3O_4 [12–14], CuO [15] and RuO_2 [16] provide a good promising to substitute conventional carbonaceous materials due to their high theoretical capacities. For example, Co_3O_4 can store more than eight lithium atoms per formula unit, corresponding to a reversible capacity of 890 mAh g^{-1} [9–11,17]. Unfortunately, most of the transition-metal oxides suffer from the problem of poor cycle performance, on one hand resulting from the large specific volume change during cycling process which leads to the aggregation of metal oxide and even pulverization of the electrode [10,18], on the other hand forming the unstable solid electrolyte interface (SEI) film on the surface of transition-metal oxides [18,19]. It has been demonstrated that the thick SEI films formed on the surface of metal oxides during discharge process could be completely decomposed by the catalysis of transition metals upon lithium extraction, which not only leads to rapid capacity decay of transition-metal oxides but also to severe safety problem for lithium ion batteries [18,19].

Recently, several strategies have been proposed to improve the cycle performance of transition-metal oxides by decreasing the particle size [20,21], using the metal oxide films or alloys [19,20], or dispersing metal oxides into an inactive/active matrix [18,22,23]. One of the most promising strategies is to disperse nanosized transition-metal oxides into a carbon matrix, where carbon acts as both structural buffer and electrochemically active material during the lithium insertion/extraction [9–12,18]. For example, CuO/graphite [24] and Co_3O_4/porous carbon composites [9,25,26] with high capacity and improved cyclability were achieved as anode materials for lithium ion batteries. However, it is still a challenge to provide enough void volume to compensate the volume change of transition-metal oxides and at the same time to avoid the direct contact of transition metal with SEI films during cycling processes, which is very important to improve the cycle performance and safety of transition-metal oxides.

In our present works, we design and elaborate a new type of monodisperse hollow carbon spheres with encapsulation of Co_3O_4 nanoparticles (denoted as HCSE-Co_3O_4) via layer-by-layer coating, in which hollow carbon spheres not only could provide enough

* Corresponding author at: State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, PR China. Tel.: +86 21 64252924; fax: +86 21 64252914.
** Corresponding author.
E-mail addresses: zhanliang@ecust.edu.cn (L. Zhan), sy13@rice.edu (S. Yang).

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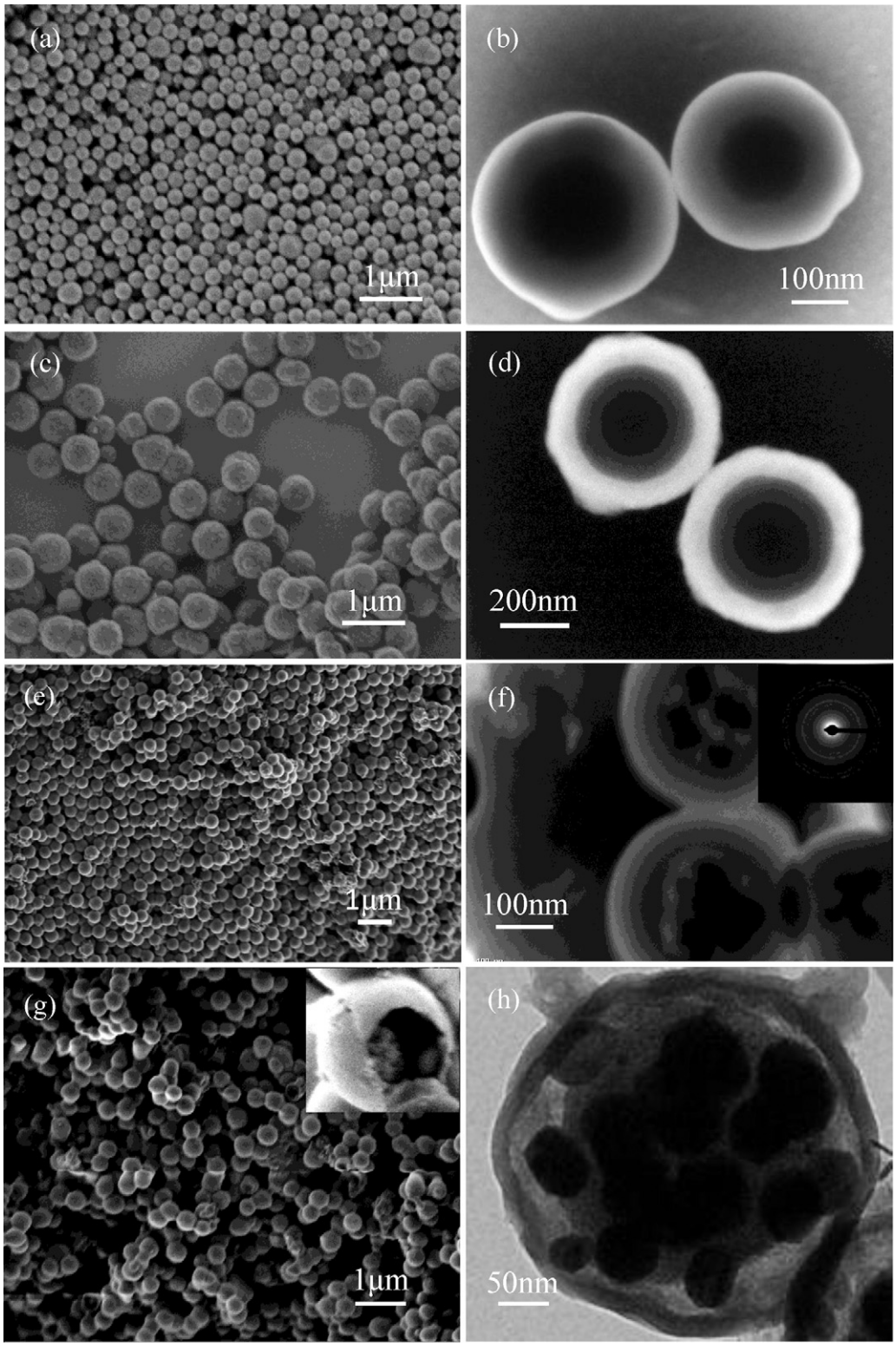

Fig. 1. SEM and TEM images of (a) and (b) cobalt alkoxide@silica, (c) and (d) cobalt alkoxide@silica@PDVB, (e) and (f) cobalt@silica@carbon and (g) and (h) HCSE-Co_3O_4. The inset in (f) is the SAED pattern of HSE-Co.

void volume to accommodate the volume change of cobalt oxide but also could effectively prevent the SEI forming on the surface of Co_3O_4 nanoparticles and the aggregation of Co_3O_4 nanoparticles during charging and discharging processes. One thus expects highly reversible capacity, excellent cycle performance and high safety of the HCSE-Co_3O_4 composite as anode materials for lithium ion batteries.

2. Experimental

2.1. Synthesis

The overall fabrication procedure of HCSE-Co_3O_4 is shown in Scheme 1. The overall synthetic procedure of HCSE-Co_3O_4 composite mainly includes four steps. In briefly, cobalt alkoxide@silica