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Ultrathin mesoporous shell Co3O4 hollow spheres as high-performance electrode materials for lithium-ion batteries

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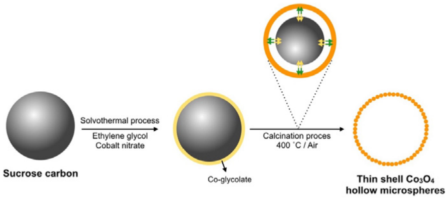
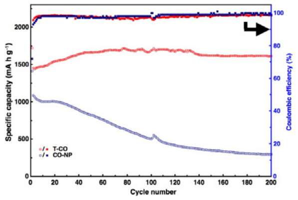
HIGHLIGHTS

- Ultrathin mesoporous shell Co_3O_4 hollow spheres are prepared using a carbon template.
- Wide voids alleviate severe volume change.
- Highly mesoporous interfacial spaces provide numerous reaction sites.
- Thin shells and wide voids enhance mass and charge transfer.
- T-CO shows excellent electrochemical performances with thin shell and wide void.

GRAPHICAL ABSTRACT





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ABSTRACT

Ultrathin mesoporous shell Co_3O_4 hollow spheres (T-CO) as nanostructured anode materials for lithium-ion batteries are synthesized using carbon sphere@Co-glycolate *via* a solvothermal reaction, followed by calcination process of 400 °C at a heating rate of 2 °C min^{-1}. T-CO is composed of ultrathin shell of ~45 nm thickness with highly mesoporous morphology and wide void of ~700 nm distance with vastly macroporous morphology, leading to superior electrochemical performance. T-CO delivers outstanding specific capacity of 1612 mA h g^{-1} at the 200th cycle at a high current density of 1.5 A g^{-1} without any apparent capacity fading. Moreover, with the increase in 10 cycles, T-CO delivers 1560, 1620, 1650, 1640, 1460, 1010, and 635 mA h g^{-1} at the various current densities of 0.5, 1, 1.5, 2.5, 5, 8 and 10 A g^{-1}, and then still maintains around 1320 mA h g^{-1} at 1.5 A g^{-1} at the 90th cycle. The reasons for showing superior electrochemical performance are as follows: (i) ultrathin mesoporous shell and wide void facilitating the redox reaction, (ii) ultrathin shell with highly mesoporous morphology increasing electrochemical sites, and (iii) wide void accommodating severe volume change and storing electrolyte for facile mass transfer; thereby maintaining the morphological integrity.

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1. Introduction

Transition metal oxides (M_xO_y, M = Co, Fe, Mn, and Cu) are known as promising anode materials in lithium-ion batteries due to their high theoretical specific capacity [1–4]. Among them, Co_3O_4 with a well-known mixed valence, which has a normal spinel structure with Co^{2+} ions in tetrahedral interstitial sites and Co^{3+} ions in the octahedral interstitial sites, is a remarkable candidate in applying nanostructured anode materials for lithium-ion batteries [5,6]. Its theoretical capacity of 890 mA h g^{-1} is nearly three times as high as that of graphite (372 mA h g^{-1}) owning to its eight-electron transfer reaction during cycling [7–9].

However, Co_3O_4 in the practical use exposes problems such as steep capacity fading and bad cycling retention due to its severe volume change and pulverization. The disclosed drawback gives rise to poor electrochemical contact and deterioration of Co_3O_4 during lithiation/delithiation [10]. The guarantee of superior electrochemical performance involving high specific capacity, excellent rate capability, and exceptional cycling stability is related to its nanostructured morphology [2,11–14]. Excellent specific capacity is mainly dependent on how fast the redox reaction progresses. High rate capability is governed by the rate of charge transfer, which is the ability of electrochemical reaction of ions and electrons in the interface between the electrode and the electrolyte [15,16]. Meanwhile, exceptional cycling stability relies on the structural integrity accommodating volume expansion and contraction during by lithiation/delithiation [17]. The desire for superior electrochemical performance might be satisfied by designing thin hollow metal oxide microspheres with thin shell and wide void, which can overcome pulverization and deterioration of Co_3O_4 from huge volume expansion during lithiation/delithiation [18,19]. The preparation of metal oxide hollow spheres using sucrose-based carbon as a sacrificial template has been widely attracted because they improve the electrochemical performance with excellent cycling retention by facilitating mass transfer and charge transfer as a result of maintaining the structural integrity by alleviating volume expansion [20].

Ultrathin mesoporous shell Co_3O_4 hollow spheres are synthesized as follows: (i) Formation of carbon sphere@metal-glycolate by a solvothermal process of the composite solution of cobalt nitrate and carbon microspheres in ethylene glycol. (ii) Synthesis of ultrathin mesoporous shell Co_3O_4 hollow spheres from carbon sphere@metal-glycolate by a calcination process at a proper temperature. During calcination process, temperature gradient (ΔT) generates ultrathin mesoporous shell Co_3O_4 hollow spheres by inducing the heterogeneous contraction with non-equilibrium thermal balances. Ultrathin mesoporous shell Co_3O_4 hollow spheres are synthesized through the mutual cooperation of inward ripening involving the adhesive force (F_a) and outward ripening involving the cohesive force (F_c) [21–23]. To our knowledge, it is hard to find elsewhere systematic research on the synthesis of ultrathin mesoporous shell hollow Co_3O_4 sphere.

We design ultrathin mesoporous shell Co_3O_4 hollow spheres (T-CO) using a carbon sphere template with the effect of calcination temperature to acquire superior electrochemical performance without any capacity decay. The Co_3O_4 hollow microspheres with highly mesoporous thin shell and wide void enable electrodes to offer outstanding rate capability and excellent capacity retention by alleviating volume expansion [24–28]. The architecture of T-CO with mesoporous thin shell and macroporous wide void plays important roles in facilitating mass transfer and charge transfer, and sustaining structural integrity, which leads to the superior electrochemical performance.

2. Experimental

2.1. Synthesis of sucrose carbon spheres

25 g sucrose (M_W: 342.30, Alfa Aesar, Korea) as a carbon precursor was completely dissolved in 50 ml deionized water, and then moved into a 180 ml Teflon-lined stainless steel autoclave. The sealed autoclave was hydrothermally reacted at 190 °C for 3 h. After cooling down to room temperature, the resulting product as a black precipitation was collected by the filtration, and rinsed with distilled water several times to remove any impurities. Finally, sucrose-based carbon spheres were obtained after drying at 80 °C for 12 h.

2.2. Ultrathin mesoporous shell Co_3O_4 hollow spheres and Co_3O_4 nanoparticles

1 mmol of cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) was dissolved in 60 ml of ethylene glycol (EG), thoroughly dispersed 0.6 g of carbon microsphere, and then completely mixed the composite solution by ultrasonication for 2 h. The homogeneous solution was moved into a 180 ml Teflon-lined stainless steel autoclave. The sealed autoclave was reacted at 180 °C for 12 h, and then cooled down to room temperature. The black precipitation was collected by vacuum filtration, rinsed with distilled water several times, and then dried at 80 °C for 12 h. In this solvothermal reaction, EG serves as a solvent as well as a reduction reagent [29]. In order to obtain ultrathin mesoporous shell Co_3O_4 hollow spheres, the obtained product was calcined at 400 °C for 3 h at a heating rate of 2 °C min^{-1} in air, which was denoted as T-CO. In comparison of T-CO, Co_3O_4 nanoparticles were prepared using the same method mentioned above without carbon spheres, which were labeled as CO-NP.

2.3. Characterization

The surface morphologies of as-prepared samples were analyzed by field emission scanning electron microscopy (FE-SEM, S-4700, Hitachi Japan). The determination of crystallinity was investigated by X-ray diffraction (XRD, D/MAX Ultima III, Rigaku, JAPAN). The nanostructured morphology and elemental mapping of the samples were examined by transmission electron microscopy (TEM, TECNAI F20, Philips, Netherlands) with X-ray energy-dispersive spectroscope in the Korean Basic Science Institute (KBSI, Gwangju center). The porous characteristics of the samples were verified at 77 K in nitrogen atmosphere by Brunauer-Emmett-Teller (BET, Micromeritics ASAP2020, USA) method.

2.4. Electrochemical performance

The electrochemical tests of the as-prepared samples were studied at room temperature by using coin cells (type CR2032). The working electrodes were prepared using the as-prepared active materials, carbon black, and poly(acrylic acid) (PAA, M_W: ~450,000, Aldrich) in a weight ratio of 70:15:15 in N-methyl pyrrolidinone (NMP) solution to form a slurry. The slurry was pasted on a copper foil and dried in an oven at 80 °C for 12 h. The cells were assembled in an argon glovebox. The lithium metal foil was used as counter and reference electrodes, a polypropylene film membrane (Celgard® 2400) as a separator, and 1 M $LiPF_6$ (DMC/EC, 1:1 by volume) as electrolyte. The loading densities of electroactive materials for cycle performances were ~0.9 mg cm^{-2}. The galvanostatic charge/discharge tests were carried out with a battery testing system (WBCS 3000, Won-A Tech., Korea) between 0.01 and 3 V at various