



One-pot synthesis of CoO/C hybrid microspheres as anode materials for lithium-ion batteries

Hui Qiao^a, Lifen Xiao^{a,*}, Zhi Zheng^b, Haowen Liu^c, Falong Jia^a, Lizhi Zhang^{a,*}

^a Key Laboratory of Pesticide & Chemical Biology of Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, People's Republic of China

^b Institute of Surface Micro and Nano Materials, Xuchang University, Xuchang 461000, People's Republic of China

^c Key Laboratory of Catalysis and Materials Science of Hubei Province, College of Chemistry and Materials Science, South-Central University for Nationalities, Wuhan 430074, People's Republic of China

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ABSTRACT

We report a one-pot method to synthesize CoO/C hybrid microspheres via a solvothermal approach. The resulting samples were characterized by thermogravimetric analysis, X-ray diffraction, X-ray photoelectron spectroscopy, field-emission scanning electron microscopy, transmission electron microscopy and charge–discharge test. X-ray diffraction analysis revealed that the as-prepared samples possessed poor crystalline characteristics and were transformed into crystalline materials after thermal treatment. Field-emission scanning electron microscope images showed that the surfaces of these as-prepared spheres were relatively smooth and of about 2.2 μm in diameter. The diameters of the spheres kept unchanged after being annealed at 800 °C in a high purity nitrogen atmosphere under ambient pressure. The preliminary electrochemical test found that the annealed CoO/C hybrid microspheres exhibited an ultrahigh initial discharge capacity of 1481.4 mAh g^{-1} in the potential range of 3.0–0.01 V. This value was much higher than that of CoO nanoparticles. Although the capacity of the second discharge cycle decayed to 506.2 mAh g^{-1} , the annealed CoO/C hybrid microspheres anode exhibited very stable reversible capacity at about 345 mAh g^{-1} only after 10 cycles. This rapid stabilization ability was attributed to the matrix effect of carbon, which may effectively prevent the aggregation of small particles during charging–discharging process.

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1. Introduction

Nanostructured transition metal oxides have received great interest in lithium-ion batteries [1–7]. The electrodes made of transition metal oxides (MO, where M is Co, Ni, Cu, or Fe) nanoparticles demonstrated high electrochemical capacities (about 700 mAh g^{-1}), great capacity retention, and high recharging rates [1,2]. More importantly, the mechanism of Li reactivity to these transition metal oxides differs from the classical Li insertion/deinsertion in graphite anodes or Li-alloying processes in alloy electrodes. The mechanism involves the formation and decomposition of Li_2O , accompanied by the reduction and oxidation of metal nanoparticles, respectively. Although these nanostructured transition metal oxides are so attractive because of their high capacities, their commercial use is still hindered. The most critical problem is

their large specific volume change, resulting in the aggregation of small particles into larger particles in the host matrix during the insertion and deinsertion of Li [3–7]. This causes rapid anode disintegration under the induced mechanical stress and capacity fading upon cycling [8–11]. One way to overcome the volume changes during Li^+ insertion and extraction is to embed the active material in a cushioning medium which maintains particle connectivity, even after pulverization. This medium can be electrochemically active or inactive. A well-known medium is the amorphous carbon or graphite. For example, the fabrication of tin oxide–carbon/graphite anode materials realized the above idea [12–14]. These anode materials showed better electrochemical performances than pure tin oxide anode. Huang et al. reported that graphite–metal oxide composites show a discharge capacity of 347 mAh g^{-1} [15]. Recently, Li and coworkers reported that a one-pot synthesis of oxides @ C core–shell nanostructures via a hydrothermal method. They found that the calcined SnO_2 @ C core–shell nanostructures showed unusual reversible Li storage capacities [16].

In this study, for the first time we report that CoO/C hybrid microspheres can be prepared via a solvothermal approach. These

* Corresponding authors. Tel.: +86 27 6786 7535; fax: +86 27 6786 7535.

E-mail addresses: lfxiao@mail.ccnu.edu.cn (L. Xiao), zhanglz@mail.ccnu.edu.cn (L. Zhang).

hybrid microspheres are different from these reported oxides @ C core-shell nanostructures [16].

2. Experimental

2.1. Preparation of amorphous CoO/C hybrid microspheres

0.238 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (AR) was added to 18 mL of distilled ethanol. Then 0.198 g glucose was added to the above solution. The resulting solution (initial pH 4.8) was transferred to a 22-mL Teflon-lined autoclave and stored at 180°C for 24 h, then air-cooled to room temperature. The as-prepared product (denoted as CC) were washed several times with distilled ethanol, and finally dried at 60°C in a vacuum-oven. For comparison, we also prepared a sample from the solution with initial pH of 7 by adding sodium hydroxide.

2.2. Preparation of crystalline CoO/C hybrid microspheres

The amorphous sample prepared via solvothermal reaction was annealed in the tube furnace at 800°C in a high purity nitrogen atmosphere under ambient pressure. Then the furnace was naturally air cooled to room temperature under the protection of nitrogen.

2.3. Characterization

X-ray diffraction patterns (XRD) of the products were recorded on a X-ray diffractometer (MAC Science Co. Ltd., MXP 18 AHF) with monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) was conducted on a thermogravimetric analyzer TGA 2050, under an air flow of 100 mL min^{-1} with a heating rate of $10^\circ\text{C min}^{-1}$ from room temperature to 800°C . X-ray photoelectron spectroscopy (XPS) measurements were performed in a VG Scientific ESCALAB Mark II spectrometer equipped with two ultra-highvacuum (UHV) chambers. All the binding energies were calibrated to the C 1s peak at 284.8 eV of the surface adventitious carbon. Field-emission scanning electron microscope (FE-SEM, JSM-5600) was used to characterize the morphology of microspheres. Transmission electron microscopy (TEM) was performed on a transmission electron microscopy (Philip CM 120) at an accelerating voltage of 120 KV.

2.4. Electrochemical measurement

Electrodes were prepared by coating a copper foil substrate with the slurry of the active materials (80 wt%), carbon black (10 wt%), and poly(vinylidene fluoride) (10 wt%) dissolved in cyclopentanone. After coating, the slurry was dried at 100°C for 12 h and then pressed between two stainless steel plates at 1 MPa. Prior to cell assembling, the electrodes with area of 0.64 cm^2 were dried at 120°C for 4 h under vacuum. The testing cells had a typical two-electrode construction using a polypropylene microporous sheet as the separator, and 1 M LiPF_6 dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v) are used as the electrolyte. A pure lithium foil was used as the negative electrode and the annealed CoO/C hybrid microspheres film was used as the working electrode, respectively. The cells were assembled in an argon-filled glove box. Charge-discharge tests were carried out at a constant current density of 30 mA g^{-1} in a range of 3.0–0.01 V vs. Li/Li^+ . All the tests were performed at room temperature.

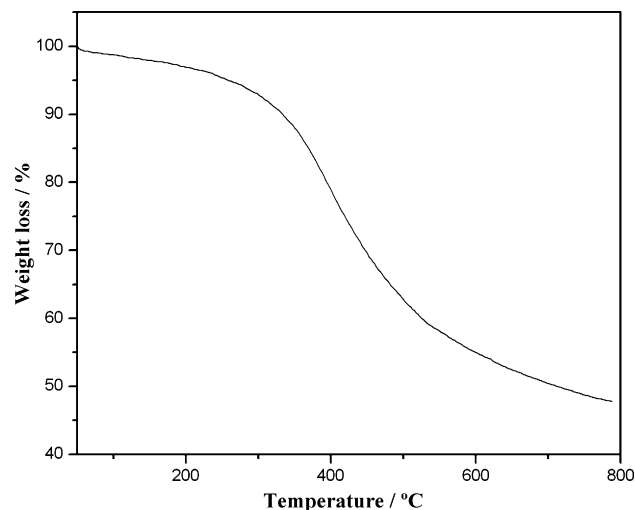


Fig. 1. Thermogravimetric curve of the as-prepared CC sample.

3. Results and discussion

3.1. TG analysis

Fig. 1 shows thermogravimetric curve of the as-prepared CC sample prepared via the solvothermal reaction. From TGA measurements, it is seen that the as-prepared sample loses weight in one step between 100 and 700°C in the TGA curve. The weight loss is 45.9% for the as-prepared CC sample. This weight loss could be attributed to the evaporation of physically absorbed water and residual solvent in the samples. It is known that water in the electrode material creates challenges in lithium battery application because of the instability of lithium with water and the decomposition of water during the charge/discharge processes [1]. Therefore, TGA analysis provides us the thermal treatment conditions for the subsequent charge-discharge test of the resulting sample.

3.2. XRD patterns

The crystal structures of the resulting products were examined by X-ray diffractometry (XRD). Fig. 2 shows the typical XRD patterns

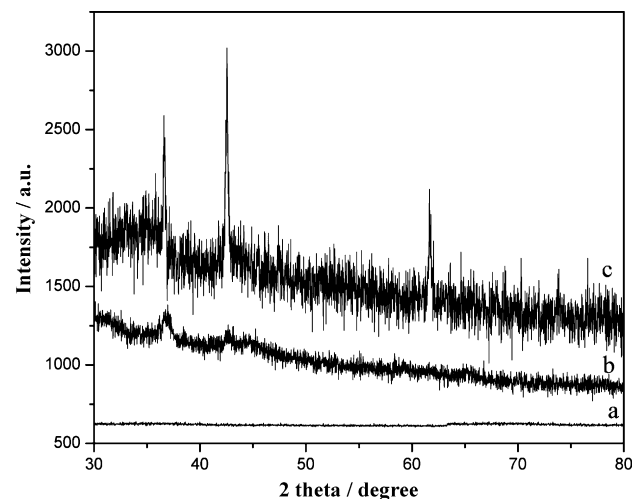


Fig. 2. XRD patterns of as-prepared and annealed CC samples. (a) As-prepared amorphous CoO/C hybrid microspheres; (b) annealed in nitrogen atmosphere at 300°C ; (c) annealed in nitrogen atmosphere at 800°C .

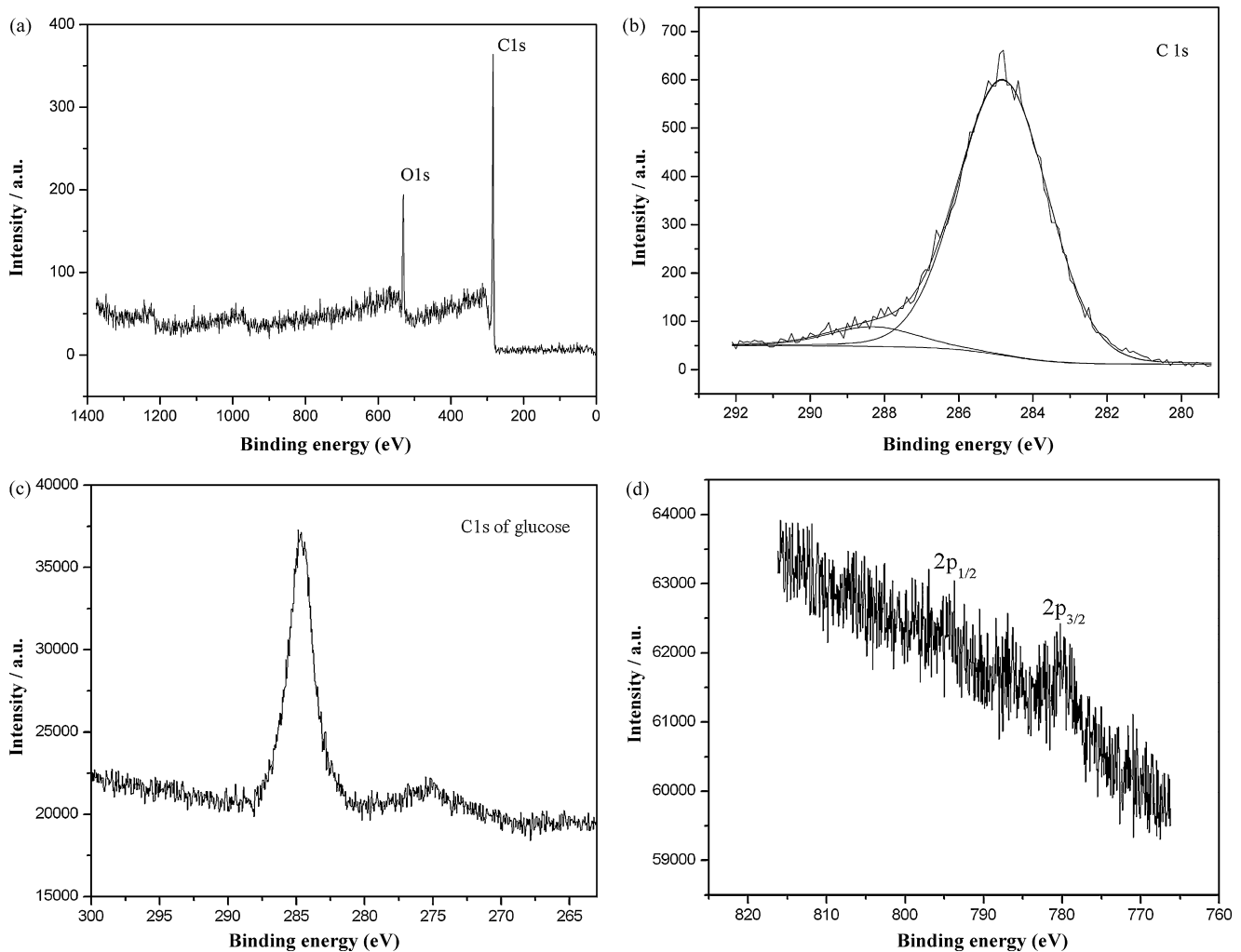


Fig. 3. XPS spectra of (a) survey, (b) C 1s of the as-prepared CC sample, (c) C 1s of the raw glucose, and (d) Co 2p of the annealed sample.

of as-prepared and annealed CC samples. Fig. 2a reveals the amorphous nature of the as-prepared sample. This amorphous sample could be transferred into crystalline materials after annealing in nitrogen. Obviously, annealing temperature affected the samples crystallization. Higher annealing temperature resulted in higher crystallinity of cobalt oxide in the annealed CC sample. When the amorphous sample was thermally treated at 300 °C in N₂ atmosphere, peaks from the CoO phase (JCPDS File No. 78-0431) appeared (Fig. 2b). After thermally treated at 800 °C in N₂ atmosphere, well-defined XRD patterns of cubic CoO phase was observed (Fig. 2c). The lattice constants of CoO phase can be calculated as follows: $a = b = c = 4.262(5) \text{ \AA}$, and $\alpha = \beta = \gamma = 90^\circ$, which are consistent with the literature values [1,17].

3.3. XPS spectra

X-ray photoelectron spectroscopy was used to investigate the surface chemical composition of the as-prepared and after annealing sample. XPS survey spectrum of the as-prepared CC sample revealed that the sample contained O and C (Fig. 3a). The core level high-resolution spectra of C 1s and O 1s regions were also investigated by XPS. The broad peak of C 1s could be fitted by two peaks at the binding energies of 284.8 and 288.5 eV for the as-prepared CC sample (Fig. 3b). The dominant peak (284.8 eV) was thought to signal the presence of elemental carbon and the peak (288.5 eV)

indicated the presence of carbon atoms bound to two oxygen atoms (COO-like). The strong signal of elemental carbon should not only arise from adventitious carbon, but also from the carbon reduced from glucose. The later peak arisen from the adsorbed species at the surface, as reported by Dedryvere [9]. Fig. 3c is the core level high-resolution spectra of C 1s of the raw glucose. The absence of C 1s characteristic peaks of glucose in Fig. 3b ruled out the presence of residual glucose in the as-prepared CC sample. No cobalt signal on XPS spectrum of the as-prepared CC sample suggested the nanosphere surface was composed of amorphous carbon thicker than 10 nm because the XPS could only detect the photoelectrons from outer surface of 10 nm. After thermally treated at 800 °C in N₂ atmosphere, the XPS signals of Co 2p were observed at binding energies at around 780.2 (Co 2p_{3/2}) and 794.5 eV (Co 2p_{1/2}) (Fig. 3d), confirming the existence of CoO in the annealed sample. Therefore, we concluded that the annealed sample consisted of CoO and amorphous C on the basis of XRD and XPS results.

3.4. SEM and TEM images

The morphologies of the as-prepared samples were investigated by field-emission scanning electron microscopy. We found the as-prepared sample consisted of spherical particles (Fig. 4a). The sizes of these spheres were relatively uniform. Their diameters were in the range of 1.3–2.8 μm. The surfaces of these spheres were rela-

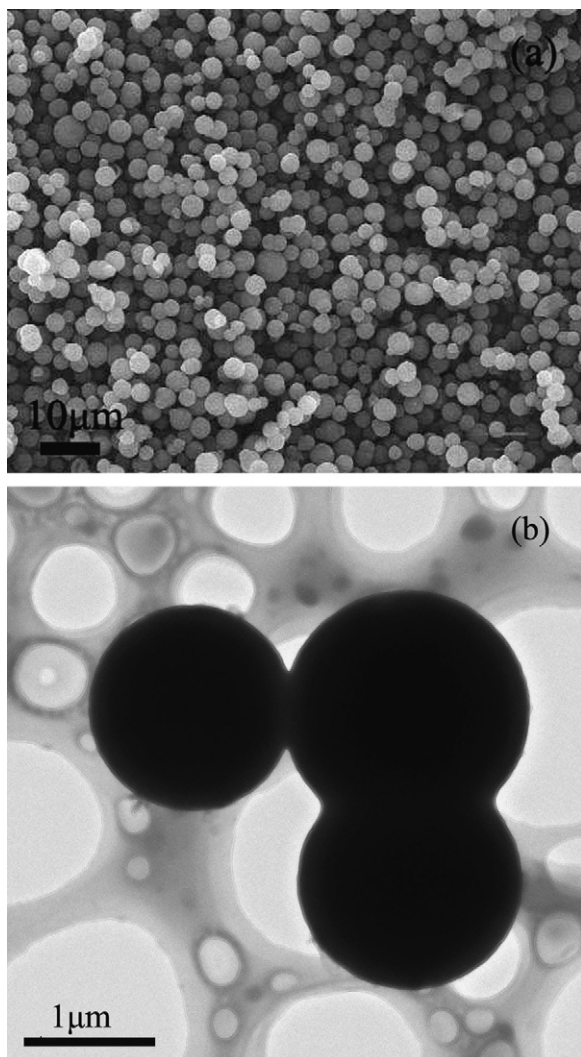


Fig. 4. FE-SEM (a) and TEM (b) images of the as-prepared CoO/C hybrid microspheres.

tively smooth. A typical TEM image (Fig. 4b) further confirms the spherical morphology of the as-prepared sample. Different from the previous study [16], core-shell structures could not be observed in the as-prepared materials according to TEM observation. Fig. 5 shows the FE-SEM and TEM images of CoO/C hybrid microspheres after annealing in nitrogen atmosphere at 800 °C. The sizes of these spheres kept unchanged after annealing (Fig. 5a). Fig. 5b further confirms the spherical morphology of the annealed CoO/C hybrid materials. In this study, the core-shell structures were not observed from TEM images, suggesting that CoO nanoparticles were homogeneously distributed in the carbon spherical matrix. This is different from the results reported by Sun et al. [16]. They obtained oxides @ C core-shell structures with carbonaceous polysaccharide shells and oxides (including hydroxides or complex oxides) cores via a one-pot hydrothermal method.

3.5. Formation of CoO/C hybrid microspheres

Hyeon and coworkers synthesized hollow tin dioxide (SnO_2) microspheres by the heat treatment of a mixture composed of tin(IV) tetrachloride pentahydrate and resorcinol-formaldehyde gel. They found that micrometer-sized spherical particles are known to form in the low pH condition, while three-dimensional

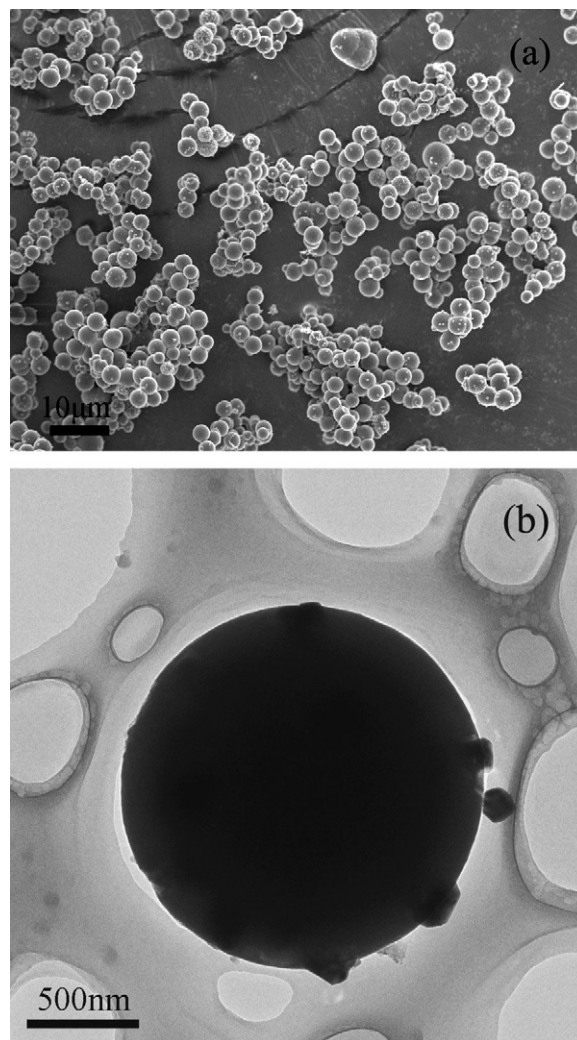


Fig. 5. (a) FE-SEM image and (b) TEM image of CoO/C hybrid microspheres annealed in nitrogen atmosphere at 800 °C.

(3D) interconnected nanostructures composed of nanoparticles are produced at high pH value [18]. In our study, the initial pH value of the reaction mixture of cobalt chloride and glucose was 4.8. This led to the formation of micrometer-sized dense spherical particles. When we adjusted the pH of the solution to 7 by adding sodium hydroxide, 3D interconnected nanoparticle aggregates were produced (Fig. 6). These observations agreed well with Hyeon's results [18].

Various chemical reactions of glucose can take place under hydrothermal (or solvothermal) conditions and result in a complex mixture of organic compounds [19–22]. This makes it difficult to determine the exact chemical reaction in the sealed vessel. We found that no solid products formed if only glucose was solvothermally treated in the absence of metal salts. Moreover, CoO/C hybrid spheres could not be obtained in cases of solvothermal treatment below 140 °C or at 180 °C for less than 2 h. In those cases, the formation of viscous solution with an olive-drab color indicates that some aromatic compounds and oligosaccharides were formed. It was denoted as “polymerization” by other researchers [20]. Cobalt complexes may also be present in these aromatic compounds and oligosaccharides. As reported by Sakaki et al. [20], during solvothermal reaction the breakage of these functional groups leads to the decrease in the polarity of the solution and probably causes the conversion of the water-soluble to the water-insoluble, although

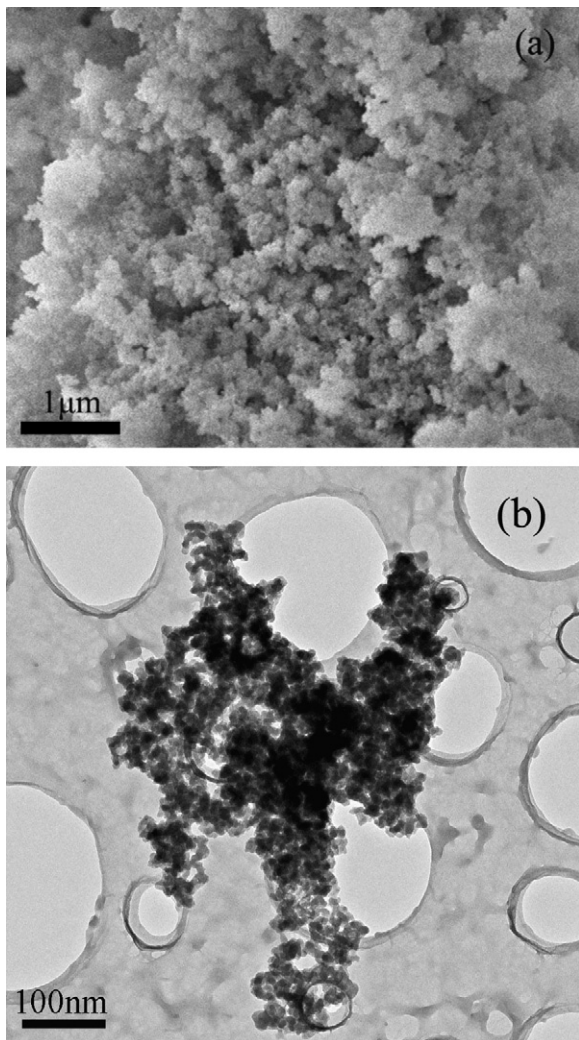


Fig. 6. FE-SEM (a) and TEM (b) images of CoO/C nanoparticles obtained from the solution with initial pH of 7.0 via solvothermal reaction.

they are ethanol-soluble. The ethanol-soluble species may be the intermediates for the CoO/C hybrid spheres. When the temperature was higher than 140 °C or the reaction time was longer than 2 h at 180 °C, the ethanol-soluble intermediates was converted to the CoO/C microspheres. On the basis of the above results, we proposed a possible mechanism for the formation of CoO/C hybrid spheres. This mechanism involves the first formation of aromatic compounds containing cobalt ions through polymerization and the subsequent formation CoO/C hybrid spheres through the simultaneous solvothermal carbonization and formation of CoO nanoparticles embedded in carbon spherical matrix.

3.6. Charge–discharge test

It is well known that CoO and hard carbon from glucose are all Li storage materials [1,17,23]. The cobalt oxide nanoparticles have a theoretical specific capacity of 700 mAh g⁻¹, which is much higher than that of already-commercialized graphite (about 350 mAh g⁻¹) [1]. The mechanism of the reaction with lithium of transition-metal oxides differs from the classical mechanisms, which are based either on reversible insertion/deinsertion of lithium into host structures or on lithium alloying reactions. This difference lies in the fact that most of these materials crystallize in a rock-salt structure that does not contain any available empty sites for Li ions. We proposed

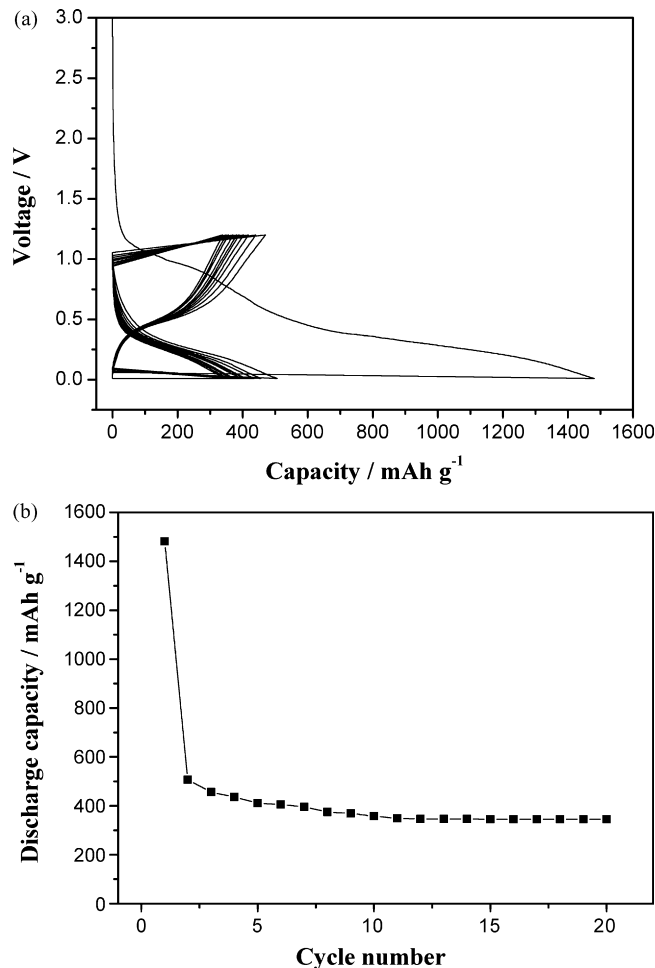
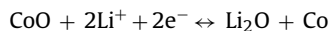


Fig. 7. The charge and discharge curve (a) as well as variation of discharge capacity vs. cycle number and (b) of CoO/C hybrid microspheres annealed in nitrogen atmosphere at 800 °C.

the electrochemical reaction mechanism of Li with cobalt oxide as follows [1].



This implies the reversible formation and decomposition of Li₂O. The utility of the electroactive material CoO would be restricted by its low electric conductivity. The carbonaceous matrix from glucose and the addition of carbon black used as the conducting agent could promote the conductivity of the electrode and the utility of the electroactive material.

The charge and discharge curve of annealed CoO/C hybrid microspheres and the corresponding variation of discharge capacity vs. cycle number are shown in Fig. 7. Elemental analysis revealed 22.9 wt% of cobalt and 70.8 wt% of carbon existed in the hybrid spheres. These hybrid microspheres showed an initial high discharge specific capacity of 1481.4 mAh g⁻¹ in the potential range of 3.0–0.01 V. The capacity was much higher than that of CoO nanoparticles (about 700 mAh g⁻¹) and graphite–metal oxide composites (347 mAh g⁻¹) [1,15], as well as theoretical value (about 450 mAh g⁻¹) of a composite material of 29.2 wt% of cobalt oxide and 70.8 wt% of carbon. The capacity of the annealed CoO/C hybrid microspheres decayed to 506.2 mAh g⁻¹ in the second cycle, a possible reason is that during the charge/discharge processes, cobalt metal may be isolated by the nonconducting materials such as Li₂O or passive film (side-reaction byproducts of water and lithium).

This assumption has already been confirmed in the previous work [24–26]. An ideal metallic nanoparticle formation is one in which the network is interconnected in the first charge/discharge cycle, because the network facilitates both charge-transfer reaction and electron conduction. The capacity decreased with the increase of the cycle numbers and reached a very stable reversible capacity at about 345 mAh g⁻¹ only after 10 cycles. It is very interesting to note that the discharge capacity of these CoO/C hybrid spheres can be stabilized only after 10 cycles. Some previous studies on CoO anode provided some hints to explain this rapid stabilization ability. It has been reported that transition metal oxides show reversible Li storage behaviors [1,2]. For the CoO/C hybrid spheres, the cobalt oxide nanoparticles are homogeneously distributed in the carbon matrix, which ensures that the formed Li₂O and Co contact well without separation. Meanwhile, the carbonaceous matrix from glucose itself has Li storage capacities and high electronic conductivity, which is able to keep CoO nanoparticles electrically connected and stabilize the CoO nanoparticles against agglomeration during charging–discharging process. These factors contribute to the high reversible capacity and excellent cycling performance. Although the capacity of CoO/C hybrid microspheres is lower than that of Co₃O₄ nanowires possessing a stabilized discharge capacities of 600 mAh g⁻¹ after 20 cycles [27], our CoO/C hybrid microspheres exhibited much better electrochemical performance than SnO₂@C core–shell nanostructures [16]. The capacity of these SnO₂@C core–shell nanostructures still inclined to decay after 40 cycles.

4. Conclusions

For the first time, we report a one-pot synthesis of CoO/C hybrid microspheres via a solvothermal approach. The preliminary electrochemical test revealed that the annealed CoO/C hybrid microspheres possessed an initial high discharge capacity of 1481.4 mAh g⁻¹ in the potential range of 3.0–0.01 V, which was much higher than that of CoO nanoparticles. Although the capacity of the second discharge cycle decayed significantly, the annealed CoO/C hybrid microspheres anode exhibited very stable reversible capacity at about 345 mAh g⁻¹ only after 10 cycles. This rapid stabilization ability was thought to be attributed to the matrix effect of carbon, which could effectively prevent the aggregation of small particles during charging–discharging process.

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