Synthesis of ZnO–ZnCo2O4 hybrid hollow microspheres with excellent lithium storage properties

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Article Info

Article history:
Received 6 February 2015
Received in revised form 7 April 2015
Accepted 8 April 2015
Available online 9 April 2015

Abstract

ZnO–ZnCo2O4 hybrid hollow microspheres are successfully produced via an annealing process of the pre-fabricated zinc–cobalt citrate hollow microspheres in air. ZnO and ZnCo2O4 have homogeneous distribution within the whole hollow microspheres. The gained hybrid hollow microspheres deliver outstanding lithium storage properties when utilized as the anode material in lithium ion batteries. A high reversible capacity of 1199 mA·h·g⁻¹ can be retained after 200 cycles. The exceptional electrochemical properties of the hybrid hollow microspheres are ascribed to the synergetic effect between ZnO and ZnCo2O4 nanoparticles, the catalytic effect of Co nanocrystals, the favorable hollow structures together with the nanometer-sized building blocks of hybrid microspheres.

Keywords:
Zinc oxide
Zinc cobalt oxides
Hybrid hollow microspheres
Anodes
Lithium ion batteries

1. Introduction

In the past decades, lithium ion batteries have been deemed as one of the most promising energy storage devices in the fields of portable electronics, electric vehicles and hybrid electric vehicles in terms of their long cycling time, large energy density and no memory effect [1–8]. The traditional graphite anodes could not satisfy the ever-growing large energy requirements in the current society owing to their relatively low theoretical capacity of 372 mA·h·g⁻¹ and safety issue. Seeking for alternative electrode materials has triggered widespread research interest in recent years. Compared to conventional carbonaceous materials, transition metal oxides have been paid great attentions for using as the anode material in lithium ion batteries in view of their higher theoretical capacity [9–18]. Although great progresses have been made, the electrochemical performances of many binary metal oxides are still unsatisfactory due to their intrinsic characteristics including poor electrical conductivity and ion diffusion kinetics together with huge volume variation during the repetitive lithium uptake/removal process. Recently, studies have demonstrated that ternary transition metal oxides with AB2O4 spinel structures can address the aforementioned shortcomings to some extent due to the reinforcement or synergetic effect between different constituent. For example, various ternary transition metal oxides including NiFe2O4, CuCo2O4, ZnCo2O4, (Mg, Cu)-codoped ZnFe2O4 and so on, have been successfully prepared and reveal good electrochemical properties when applied as the anode materials for lithium ion batteries [19–24]. Among them, ZnCo2O4, the partial replacement of Co element in Co3O4 by cheaper and nontoxic Zn element, holds bright prospects as the advanced electrode materials not only because Zn and Co elements can function as mutual favorable buffering matrices to alleviate the large mechanical stress derived from the severe volume change during cycling, but also because Zn can further reversibly react with Li through alloying/dealloying reactions to contribute to extra capacity. Up to date, various ZnCo2O4 materials such as nanoparticles, nanotubes, yolk–shell microspheres and feather-like nanostructures have been fabricated and employed as the anode materials for lithium ion batteries [22,25–28].

Very recently, mixed metal oxides have been intensively applied as the advanced anode materials for lithium ion batteries since the number of ternary transition metal oxides which have a single phase is greatly limited [29–34]. The synergetic effect between the different metal oxides is helpful in further increasing the lithium storage performances of electrode materials. For example, Fe2O3@NiO core/shell nanorod arrays prepared by Tu's group demonstrated better lithium storage properties than individual Fe2O3 and NiO electrodes [29]. It was pronounced that the special structural stability could be realized for hybrid nanorod arrays by combining the Fe2O3 cores and ultrathin NiO shells, accounting for their superior electrochemical properties. Three-dimensional branched CuO/Co3O4 core/shell nanowire
heterostructures were produced by Li's group through a simple thermal oxidation approach, which revealed the greatly enhanced cycling stability on the basis of the synergetic effect between CuO and Co₃O₄ [32]. Unfortunately, most of mixed metal oxides reported previously show the branched configurations and there are few literatures concentrating on the fabrication of mixed metal oxides with hollow structures and their lithium storage properties. In addition, the conventional “two-step” strategy for the fabrication of the mixed metal oxides with branched structures, that is to firstly prepare the core materials combined with subsequent synthesis of shell materials, is complicated and tedious. Consequently, it is of great significance to produce mixed metal oxides with hollow structures through a simple approach, which may demonstrate the exceptional lithium storage properties.

In this work, well-dispersed ZnO–ZnCo₂O₄ hybrid hollow microspheres are produced for the first time through an annealing treatment of the pre-synthesized zinc–cobalt citrate hollow microspheres in air. Based on their unique structural features, the prepared hybrid hollow microspheres depict high specific capacity, extraordinary cycling stability and exceptional rate capability when applied as the anode materials for lithium ion batteries. After 200 cycles, well-dispersed ZnO–ZnCo₂O₄ hybrid hollow microspheres deliver a high reversible capacity of about 1199 mA h g⁻¹ at a current density of 200 mA g⁻¹. The reasons for the excellent lithium storage properties of hybrid hollow microspheres are discussed in detailed.

2. Experimental

2.1. Synthesis

Zinc citrate hollow microspheres were firstly fabricated on the basis of our earlier literature [35]. 30 ml of 0.3 M cobalt nitrate solution containing 0.06 g of zinc citrate hollow microspheres was ultrasonicated for 10 min with subsequently aging treatment at room temperature for 1 h. After that, the pink zinc–cobalt citrate precipitate was acquired, rinsed with deionized water for three times and dried at 70 °C overnight. The weight of the harvested zinc–cobalt citrate hollow microspheres is about 0.0423 g and the yield is 70.5%. By annealing the obtained zinc–cobalt citrate hollow microspheres at 500 °C for 2 h in air, ZnO–ZnCo₂O₄ hybrid hollow microspheres (about 0.0311 g) could be obtained.

2.2. Characterizations

X-ray diffraction (PANalytical X’pert PRO x-ray diffractometer, Cu Kα radiation 40 kV, 30 mA), scanning electron microscopy (Hitachi SU-70), transmission electron microscopy (JEM-2100, 200 kV), Fourier-transform infrared test (Nicolet Nexus-670 FT-IR spectrometer), thermogravimetric (TG) measurement (SDT-Q600 thermal analyzer) and the specific surface area evaluations (TriStar 3020 system) were carried out to detailly characterize the harvested zinc–cobalt citrate precursor and ZnO–ZnCo₂O₄ hybrid hollow microspheres.

2.3. Electrochemical evaluations

The anode was prepared by coating a homogeneous slurry containing 70 wt% of ZnO-ZnCo₂O₄ hybrid hollow microspheres (active materials, 0.21 g), 20 wt% of acetylene black and 10 wt% of poly (vinyl difluoride) (PVDF) to copper foil (d = 16 mm) combined with subsequent drying treatment at 80 °C overnight under vacuum condition. The coating weight of active materials in the working electrode is 1.8–2.0 mg and the geometrical area of the electrode is about 2.01 cm². 1 M LiPF₆ in ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1, v/v) was applied as the

Fig. 1. The SEM (a-b) and TEM (c-d) images of zinc–cobalt citrate hollow microspheres.
electrolyte. Lithium foil and Celgard 2400 respectively serve as the counter and reference electrode, and separator. Coin-type 2025 cells were assembled in a glove box filled with argon. The cycling and rate performances were carried out on a Neware battery tester. Cyclic voltammetry profiles were collected on an Autolab electrochemical workstation.

3. Results and discussion

3.1. Morphology and structure characterizations

Fig. 1 exhibits the SEM and TEM images of the obtained zinc–cobalt citrate precursor. Apparently, the precursor is dominated by the dispersed microspheres with an average diameter of about 1.7 μm (Fig. 1a). The SEM micrograph at a higher amplification factor (Fig. 1b) shows the coarse and loose surface of microsphere. The microspheres contain Zn, Co, O and C elements (Fig. S1), indicating the successful adsorption of cobalt ion on the surfaces of zinc citrate hollow microspheres. The hollow structures of the acquired zinc–cobalt citrate microspheres are testified from the TEM observations (Fig. 1c–d). From XRD pattern, the obtained zinc–cobalt citrate precursor is mainly amorphous (Fig. 2a). FT-IR characterization displayed in Fig. 2b suggests the presence of carboxylate acid groups (−COO−, peaks around 1574.5 and 1398.2 cm⁻¹) and hydroxide groups (−OH, peak nearby 3424 cm⁻¹) in precursor. With all of above observations in mind, the successful fabrication of zinc–cobalt citrate hollow microspheres can be easily realized through a simple aging process of zinc citrate hollow microspheres in cobalt nitrate solution. The TG measurement of zinc–cobalt citrate hollow microspheres is revealed in Fig. S2. The initial weight loss below 200 °C relates to the loss of moisture in sample and the following large weight loss between 230 and 305 °C is associated with the decomposition of zinc–cobalt citrate to ZnO–ZnCo₂O₄ hybrids. Thus, the calcination temperature is determined to be 500 °C, at which zinc–cobalt citrate could be completely transformed to ZnO–ZnCo₂O₄ hybrids. XRD pattern (Fig. 2a) of the annealed product reveals the diffraction peaks of hexagonal ZnO (JCPDS card No. 36–1451) and spinel ZnCo₂O₄ (JCPDS card No. 23–1390). The lattice parameter (a) of ZnCo₂O₄ is calculated to be about 0.81096 nm. In order to further identify the composition of the product acquired after calcination, the obtained hybrid powders were dispersed into 4.0 M NaOH solution and stirred for 6 h to selectively dissolve ZnO. No diffraction peaks resulted from ZnO can be observed from XRD pattern of the product obtained after dissolution treatment (Fig. S3a), suggesting that ZnO has been completely removed from hybrid powders. EDS measurement of the product after dissolution treatment indicates the presence of Zn, Co and O elements with a Zn/Co molar ratio of about 0.5 (Fig. S3b). SEM image (Fig. S3c) shows that the hybrid microspheres have cracked to nanoparticles after dissolution treatment. According to the above results, it is reasonable to pronounce that ZnO–ZnCo₂O₄ hybrids can be successfully prepared by calcination of zinc–cobalt citrate precursor in air and ZnCo₂O₄ nanoparticles can be harvested by selectively removal of ZnO from ZnO–ZnCo₂O₄ hybrids. According to the Scherrer equation, the main crystal sizes of ZnO and ZnCo₂O₄ nanoparticles are determined to be 12.2 and 11.3 nm, respectively.

SEM image displayed in Fig. 3a depicts that the product acquired after calcination consists of a large quantity of dispersed microspheres. From the careful SEM observations (Fig. 3b–c), the microspheres are made up of many ZnO and ZnCo₂O₄ nanoparticles with an average particle size of around 30 nm. ZnO and ZnCo₂O₄ nanoparticles contact with each other closely. The hollow structures of hybrids are perfectly maintained after heating treatment, which is evidenced from the cracked microsphere (the inset in Fig. 3a) and TEM observations (Fig. 3d–e). From high resolution TEM (HRTEM) image (Fig. 3f), the interplanar spacings are calculated to be 0.260 and 0.243 nm, which are in line with the (0 0 2) plane of ZnO and (3 1 1) plane of ZnCo₂O₄, respectively. Scanning TEM (STEM) image and the corresponding element mappings are revealed in Fig. 3g–j, from which the uniform distribution of Zn, Co and O elements can be observed clearly. Namely, ZnO and ZnCo₂O₄ nanoparticles homogeneously distribute within the whole hollow microspheres and contact with each other intimately. It is worth pointing out that the homogeneous distribution of different components in mixed metal oxides plays a key role in obtaining good lithium storage performances. The weight ratio of ZnO/ZnCo₂O₄ in the hybrid microspheres is calculated to be 1.04 from EDS measurement (Fig. S4). The BET surface area of ZnO–ZnCo₂O₄ hybrid hollow microspheres is 26.2 m² g⁻¹ determined from N₂ adsorption–desorption evaluation at 77 K (Fig. S4). The pore size distribution implies the presence of mesopores centered at 25.5 nm (the inset in Fig. S5).

According to above observations and discussions, the successful preparation of well-dispersed ZnO–ZnCo₂O₄ hybrid hollow microspheres through a simple strategy is schematically illustrated in Fig. 4. During the aging process of zinc citrate hollow microspheres in cobalt nitrate solution, cobalt ions are capable of adsorbing on the surfaces of zinc citrate hollow microspheres by means of the electrostatic interplay between the positive cobalt ions and negative carboxylate acid groups (−COO⁻), resulting in
Fig. 3. The SEM (a-c), TEM (d-e) and HRTEM (f) images of ZnO–ZnCo$_2$O$_4$ hybrid hollow microspheres. The inset in (a) is a broken microsphere. STEM image (g) and the corresponding element mappings of Co (h), Zn (i) and O (j).

Fig. 4. Schematic diagram of the successful fabrication of well-dispersed ZnO–ZnCo$_2$O$_4$ hybrid hollow microspheres.
the formation of zinc–cobalt citrate hollow microspheres. By centrifugation and rinsing to remove the excess unadsorbed cobalt ions, the harvested zinc–cobalt citrate hollow microspheres are dried and then calcined at 500 °C in air. The adsorbed cobalt ions functioned as the cobalt sources would react with zinc citrate and oxygen to produce ZnCo2O4 during heating process. And the remanent zinc citrate would simultaneously convert to ZnO. Consequently, well-dispersed ZnO–ZnCo2O4 hybrid hollow microspheres can be synthesized. The intimate contact between ZnO and ZnCo2O4 nanoparticles is favorable to strengthen the electrochemical properties of hybrid hollow microspheres.

### 3.2. Electrochemical characterizations

Exhibited in Fig. 5a is the first three cyclic voltammogram (CV) curves of the ZnO–ZnCo2O4 hybrid hollow microspheres tested at 0.1 mV s−1 in 0.01–3 V, wherein two broad and strong cathodic peaks located at 0.83 and 0.40 V can be seen clearly in the first lithium intercalation process. The peak at 0.83 V derives from the decomposition of ZnCo2O4 to metallic Zn and Co, while the peak at 0.40 V is caused by the reduction of ZnO to metallic Zn, the formation of Zn–Li alloys together with the generation of solid electrolyte interphase (SEI) layers, which are in accordance with

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**Fig. 5.** The CV curves (a), galvanostatic discharge–charge profiles (b) and cycling performance (c) of ZnO–ZnCo2O4 hybrid hollow microspheres. (d) The rate capabilities of ZnO–ZnCo2O4, ZnO hollow microspheres and ZnCo2O4 nanoparticles. (e) The galvanostatic discharge–charge profiles of single ZnO hollow microspheres.
the previous reports [27,36]. In the first anodic scan, two weak peaks nearby 0.32 and 0.73 V relate to the multistep dealloying reactions of Zn–Li alloys. And the large peaks centered at 1.7 and 2.1 V are ascribed to formation of ZnO and Co3O4, respectively [27,37]. In the subsequent cathodic sweeps, the main reduction peak potential moves to larger value (0.95 V), which is caused by the changes in phase, crystallinity and structure of electrode materials during cycling [38]. From the second cycle onwards, apart from the slight differences in peak position, ZnO–ZnCo2O4 hybrids have similar CV curves in shape with other ZnCo2O4 electrode materials reported previously [22,37]. Chowdari’s group fabricated four different ZnCo2O4 spherical particles by molten salt method and suggested that the slight differences in peak position in the CV curves of four ZnCo2O4 powders relate to their morphology and structures [22]. Additionally, in the second CV scan, the voltage hysteresis of ZnO and Co3O4 are about 0.7 and 1.2 V, respectively. The large voltage hysteresis of metal oxide electrodes on the basis of conversion reactions would greatly hinder their potential applications. Therefore, reducing the metal oxide hysteresis of the as-produced hybrid hollow microspheres is highly desirable. Previous reports have revealed that iron oxides electrodes possess slightly lower voltage hysteresis, thus fabricating ZnO–ZnFe2O4 hybrid hollow microspheres through the same method in our further work may be a good try to reduce the large voltage hysteresis [39–41]. In the subsequent cycles, the CV curves well superpose, indicative of the good reversibility of lithium storage. The electrochemical reactions of the hybrid hollow microspheres occurred during discharge/charge process are summarized as follows [22,36,39]:
\[
\begin{align*}
\text{ZnCo}_2\text{O}_4 + 8 \text{Li}^+ + 8 e^- &\rightarrow \text{Zn} + 2\text{Co} + 4 \text{Li}_2\text{O} \\
\text{ZnO} + 2 \text{Li}^+ + 2 e^- &\rightarrow \text{Zn} + \text{Li}_2\text{O} \\
\text{Zn} + x \text{Li}_2\text{O} &\rightarrow x \text{Li}_2\text{Zn} (x \leq 1) \\
\text{Co} + \text{Li}_2\text{O} &\rightarrow \text{CoO} + 2 \text{Li}^+ + 2 e^- \\
\text{CoO} + 1/3 \text{Li}_2\text{O} &\rightarrow 1/3 \text{Co}_2\text{O}_4 + 2/3 \text{Li}^+ + 2/3 e^-
\end{align*}
\]

The galvanostatic discharge–charge characterizations of ZnO–ZnCo2O4 hybrid hollow microspheres are implemented at 200 mA g⁻¹ between 0.01–3.0 V and the corresponding results are depicted in Fig. 5b. The first discharge curve contains three obvious plateaus located at 1.30, 0.98 and 0.58 V, which are ascribed to the possible formation of SEI film, the decomposition of ZnCo2O4 to metallic Zn and Co, and the reduction of ZnO to Zn, respectively, being agreement with the above CV results. The hybrid hollow microspheres deliver the original discharge/charge capacities of 1503/1021 mA h g⁻¹, leading to a Coulombic efficiency of 64.8% which is higher than that (47.7%) of single ZnO hollow microspheres synthesized by directly annealing zinc citrate hollow microspheres in air (Fig. 5e). The irreversible capacity loss at the first cycle is possibly caused by the formation of SEI film [33]. Hong’s group synthesized ZnO/ZnCo2O4 submicron rod arrays through an ammonia-evaporation-induced method, which delivered the first discharge/charge capacities of 1317/811 mA h g⁻¹ [33]. ZnO–ZnCo2O4 hybrid hollow microspheres show extra-capacity of 180–350 mA h g⁻¹ during the first cycle in comparison with ZnO/ZnCo2O4 submicron rod arrays. This phenomenon is common in other binary or ternary metal oxides electrodes and may be caused by the different preparation method of electrode materials [42,43]. The enhanced Coulombic efficiency of 93.1% in the second cycle indicates the increased reversibility of electrochemical reactions.

Fig. 5c demonstrates the cycling properties of ZnO–ZnCo2O4 hybrid hollow microspheres at 200 mA g⁻¹ within 0.01–3.0 V. For comparison, the lithium storage properties of single ZnO hollow microspheres and ZnCo2O4 nanoparticles are also tested. Obviously, both ZnO hollow microspheres and ZnCo2O4 nanoparticles demonstrate the severe capacity degradation, indicating the poor cyclabilities (Fig. S6 and Fig. S7). After 600th cycles, the specific capacities of ZnO hollow microspheres and ZnCo2O4 nanoparticles are 149 and 448 mA h g⁻¹, respectively. Differently, the reversible capacity of ZnO–ZnCo2O4 hybrid hollow microspheres gradually increases in the first 15th cycles and then decreases with cycle number. From 40th cycle onwards, the reversible capacity increases again. After 200 cycles, ZnO–ZnCo2O4 hybrid hollow microspheres deliver a high specific capacity of about 1199 mA h g⁻¹, which is higher than the theoretical capacities of ZnO (978 mA h g⁻¹) and ZnCo2O4 (900 mA h g⁻¹). This phenomenon is associated with the reversible growth and dissolution of a polymeric gel-like film on the surface of the active materials during cycling, which would deliver extra specific capacity [44,45]. Undoubtedly, ZnO–ZnCo2O4 hybrid hollow microspheres show the greatly enhanced lithium storage properties compared to single ZnO hollow microspheres and ZnCo2O4 nanoparticles. To our knowledge, this is one of the best reversible capacities among various ZnO-based or ZnCo2O4-based electrode materials reported previously (Table 1).

Table 1
The electrochemical properties of various ZnO- or ZnCo2O4-based electrode materials in lithium ion batteries.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Morphology</th>
<th>Reversible capacity /mAh g⁻¹</th>
<th>Cycles</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO/graphene</td>
<td>Nanocomposites</td>
<td>487</td>
<td>100</td>
<td>[46]</td>
</tr>
<tr>
<td>ZnO–C</td>
<td>Quantum Dots</td>
<td>1200</td>
<td>50</td>
<td>[47]</td>
</tr>
<tr>
<td>ZnO–C</td>
<td>Nanoparticles</td>
<td>654</td>
<td>100</td>
<td>[48]</td>
</tr>
<tr>
<td>ZnO–C</td>
<td>Yolk–shell/hollow/solid microspheres</td>
<td>520/427/341</td>
<td>150</td>
<td>[36]</td>
</tr>
<tr>
<td>ZnO–C</td>
<td>Hollow octahedra</td>
<td>1390</td>
<td>100</td>
<td>[49]</td>
</tr>
<tr>
<td>ZnCo2O4</td>
<td>Core-shell/hollow/solid microspheres</td>
<td>985/831/345</td>
<td>50</td>
<td>[27]</td>
</tr>
<tr>
<td>ZnCo2O4</td>
<td>Mesoporous microspheres</td>
<td>721</td>
<td>80</td>
<td>[50]</td>
</tr>
<tr>
<td>ZnO–Co3O4–NiO</td>
<td>Nanowire arrays</td>
<td>357</td>
<td>100</td>
<td>[31]</td>
</tr>
<tr>
<td>ZnO–Co3O4–NiO</td>
<td>Heterostructure rod arrays</td>
<td>900</td>
<td>100</td>
<td>[33]</td>
</tr>
<tr>
<td>ZnO–Co3O4–NiO</td>
<td>Hybrid hollow microspheres</td>
<td>1199</td>
<td>200</td>
<td>Our work</td>
</tr>
</tbody>
</table>
The unique structural characteristics exert significant effect on the excellent lithium storage properties of the obtained ZnO–ZnCo₂O₄ hybrid hollow microspheres. First, the hollow structures of hybrid microspheres can offer extra space to mitigate the huge volume variation during the repetitive lithiation/delithiation process, which is capable of preventing the pulverizations of electrodes to some extent [9]. Second, the large surface area and the presence of mesopores in hybrid hollow microspheres would respectively offer more electrochemical active sites and favor the diffusion of electrolyte, consequently benefitting to increase the reversible capacity. Third, the shortened diffusion distance of lithium ions caused by the nanometer-sized building blocks of hybrid microspheres can strengthen the electrochemical reaction kinetics, which is beneficial to rate capability. Additionally, a polymeric gel-like layer would reversibly generate and dissolve at the surface of electrode materials owing to the nanometer-sized subunits features of hybrid microspheres, which can reinforce the irreversible capacity of active materials [19,51]. Fourth, the synergetic effect between ZnO and ZnCo₂O₄ plays an important role in the good lithium storage properties of hybrid microspheres. ZnO and ZnCo₂O₄ nanoparticles well disperse within the whole hollow microspheres and contact with each other tightly. Both Zn and Co formed during discharge process would function as mutual beneficial matrices to effectively accommodate the severe volume change during lithium uptake/removal process, benefitting to the cyclability [25]. After 50 cycles, the microspherical structures of ZnO–ZnCo₂O₄ hybrids are kept well to a large extent, however, the single ZnO hollow microspheres have cracked to nanoparticles and then form the large aggregations (Fig. 6). The SEM observations well evidence the good structural tolerance of hybrid hollow microspheres. Fifth, it is well-established that Co nanocrystals formed during lithiation process show the catalytic effect to decompose Li₂O, which can contribute to extra specific capacity [52,53]. With all the merits mentioned above in mind, it is rational that the as-synthesized ZnO–ZnCo₂O₄ hybrid hollow microspheres demonstrate the high specific capacity, good cycling stability and superior rate capability.

4. Conclusions

In summary, zinc–cobalt citrate hollow microspheres are synthesized through a simple aging treatment and then calcined in air to successfully fabricate ZnO–ZnCo₂O₄ hybrid hollow microspheres. ZnO and ZnCo₂O₄ nanoparticles distribute homogeneously within the whole hollow microspheres and contact with each other closely. A high specific capacity, good cycling stability and superior rate performance are realized for the obtained hybrid hollow microspheres when applied as the anode materials for lithium ion batteries, which originate from the unique hollow configuration of hybrid microspheres, the nanometer-sized building blocks, the synergetic effect between ZnO and ZnCo₂O₄ as well as the catalytic effect of Co nanocrystals. Thus, the harvested ZnO–ZnCo₂O₄ hybrid hollow microspheres may be a good anode candidate for lithium ion batteries.

Acknowledgements

The authors gratefully acknowledge financial support from the National Basic Research Program of China (No. 2012CB933103), the National Natural Science Foundation of China (Grant Nos. 51771158 and 51371154) and the Fundamental Research Funds for the Central Universities of China (Grant no. 201312G003).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2015.04.041.

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