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Hollow $\text{Co}_3\text{O}_4$ microspheres with nano-sized shell: One-step large-scale synthesis, Growth mechanism and Supercapacitor properties

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Abstract

Hollow $\text{Co}_3\text{O}_4$ microspheres with thin spherical shell were produced with one-step method at a low hydrothermal temperature ($120 \, ^\circ\text{C}$), which could be obtained without the use of solid template, organic reagent and subsequent calcination. These hollow $\text{Co}_3\text{O}_4$ microspheres possess a diameter of ca. 500 nm and thin shell thickness of ca. 50 nm. The samples were characterized by field emission scanning electron microscope (SEM), transmission electron microscopic (TEM) and powder X-ray diffraction (PXRD). A multistep-splitting growth mechanism was proposed here to reveal the formation of hollow $\text{Co}_3\text{O}_4$ microspheres. The successful fabrication of hollow spherical morphology of these microspheres highlighted the $\text{H}_2\text{O}_2$ dosage and the nitrate concentration. The electrochemical performance tests of as-prepared samples indicated that the hollow $\text{Co}_3\text{O}_4$ microspheres exhibited ultrahigh specific capacitance of 1227, 1169, 1116, 1035 F/g at current densities of 1, 2, 4, 8 A/g, respectively. After 1000 cycles, the specific capacitance of hollow $\text{Co}_3\text{O}_4$ microspheres showed high charge/discharge reversibility and only slightly decayed...
less than 3% at a current density of 2 A/g.

1. Introduction

To meet the ever-expanding energy demand in the new industrial age, research has been intensely undertaken to explore high capacity and power substitute electrode materials of traditional carbon striving to improve the efficiency of energy utilization.\textsuperscript{1-9} Nowadays the hotspot has been focused on two main aspects: a) chemical modification and embellishment for traditional carbon becomes a common practice, for example, adopt carbon nanotubes (CNTs), graphene or other materials with high electrochemical activity seems to be one of the appropriate options; b) other pseudocapacitance materials which store energy on the basis of fast reversible redox reactions occurring within those electroactive materials owing to several oxidation states.

As a result, various transitional-metal oxides as a class of ideal materials have drawn intense attentions mainly due to their good specific capacitance,\textsuperscript{10} long cycle life and a fast redox kinetics.\textsuperscript{11} For instance, RuO\textsubscript{2},\textsuperscript{12, 13} Co\textsubscript{3}O\textsubscript{4},\textsuperscript{14} NiO,\textsuperscript{15, 16} MnO\textsubscript{2}\textsuperscript{17, 18} are considered to be the most desirable candidate materials for electrochemical capacitors (ECs) application. Recent studies revealed that Co\textsubscript{3}O\textsubscript{4} is a promising alternative choice for carbon-base materials on account of the high capacitance (theoretical value to 3560 F/g), excellent reversible redox behavior, good corrosion stability and benign environmental friendliness.\textsuperscript{19} On any condition, in order to improve the electrochemical performance of materials, seeking the design of higher specific surface area and easier electrolyte-accessibility seems to be the most possible
approach. Because the unique structures facilitate the ion diffusion and mitigate the expansion of the lattice spacing of electrode materials, countless attempts have been taken to synthesize Co$_3$O$_4$ of different morphologies such as wires,$^{20,21}$ tubes,$^{22}$ walls,$^{23}$ urchin-like structures.$^{24}$ Nevertheless, in consideration of the thermal stress influence during the continuous electrochemical test, hollow morphology may probably be the most stable structure from the point of view of structural and thermal stability. Based on this viewpoint, researchers have devoted themselves to develop hollow Co$_3$O$_4$ nanoparticles with varieties of techniques.$^{25,26}$ However, there were still obstacles block on the road of manufacturing hollow Co$_3$O$_4$ spheres in a comparatively simple and efficient way. On one hand, in Ma’s and Xiao’s teamwork, they both prepared hollow Co$_3$O$_4$ spheres or 3D hierarchical Co$_3$O$_4$twin-spheresby annealing unchin-like hollow Co(CO$_3$)$_{0.5}$(OH)$\cdot$0.11H$_2$O which acted as the precursor of morphology template$^{27}$. The spherical morphology has been damaged to some extent caused by the calcining process. On the other hand, in Sun’s latest work, they had to decorate the hollow Co$_3$O$_4$ nanospheres with graphene in the aim of improving the electrochemical performance of Co$_3$O$_4$, thus increased the application costs and complicated the preparation procedures.$^{28}$ Therefore, it still remains a huge challenge to synthesize high performance hollow Co$_3$O$_4$ spheres with a low cost and effective way.

In this article, we prepared hollow Co$_3$O$_4$ microspheres without the assist of solid template and a subsequent calcination process. As is known that for the synthesis of Co$_3$O$_4$ through various means, the oxidation of Co (II) to Co (III) remains as an
unable evaded obstacle. For purpose of solving this problem, previous researchers either adopt electrodeposition method or hydrothermal process followed by high temperature calcination. In this study, the main innovation of the synthesis hollow Co$_3$O$_4$ microspheres not only lay in taking advantages of the easy oxidation of Co(NH$_3$)$_6^{2+}$ to realize Co$^{2+}$$\rightleftharpoons$Co$^{3+}$ in low temperature (120 °C), but also paid attention to manufacturing hollow structures with help of air bubbles. Moreover, the electrochemical performances of hollow Co$_3$O$_4$ microspheres exhibited ultrahigh specific capacitance of 1227, 1169, 1116 and 1035 F/g at current densities of 1, 2, 4, 8 A/g, respectively. The supercapacitor constructed with hollow Co$_3$O$_4$ microspheres also showed an excellent reversibility with an efficiency of 97.5% after 1000 cycles at a current density of 2 A/g. The amazing electrochemical properties could be ascribed to the greatly increased active sites and greatly shortened ion diffusion distances of this hollow structure.

2. Experimental Section

2.1 Materials

Cobalt nitrate (Co(NO$_3$)$_2$, analytical grade), sodium nitrate (NaNO$_3$, ≥ 99.5%), ammonium hydroxide (NH$_3$•H$_2$O, 25%~28%), hydrogen peroxide (H$_2$O$_2$, 30%) were used. All reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. and were used as received. The deionized water used in all experiments with a resistivity of 18.2 MΩ•cm was prepared using an ultrapure water system (Millipore).

2.2 Preparation of hollow Co$_3$O$_4$ microspheres
In a typical synthesis, 10 mM Co(NO$_3$)$_2$ and 10 mM NaNO$_3$ were dissolved in 20.0 mL of deionized water to form homogeneous solution. Then 10 mL NH$_3$•H$_2$O was added dropwise to the mixed solution with constant stirring in air for about 30 mins. After the addition of 4 mL of H$_2$O$_2$, subsequently the mixture was sealed in a 200 ml teflon-lined stainless steel autoclave and transferred into a homogeneous reactor set at 120 °C for 12 h. By the time the reactor cooled to room temperature, the samples were rinsed three times with deionized water and ethanol, respectively, and dried in a conventional oven. Then the black powders of hollow Co$_3$O$_4$ microspheres were obtained.

2.3 Materials characterization

The morphologies and structures of product were analyzed by field emission scanning electron microscope (FE-SEM) and Transmission electron microscopic (TEM). FESEM characterization was performed on a JSM-7600F. TEM investigation was carried out using a high-resolution transmission electron microscope (HR-TEM, JEOL, JEM-2100F) operated at 200 kV. All samples were dispersed in absolute ethanol solution and then dropped on copper grid. Selected area electron diffraction (SAED) was also performed via the previous TEM. The phase purity of the as-prepared sample was characterized by X-ray diffraction (D/max 2550VL/PC) with Cu Kα radiation from 10° to 80° at a scanning rate of 4°/min. The X-ray tube voltage and current were set at 35 kV and 200 mA, respectively. The Raman spectrum of the samples was collected on SenterraR200-L Raman system with 532 nm diode laser excitation at room temperature.
2.4 Electrochemical measurements

The electrochemical studies were performed in a conventional three-electrode system with a KOH electrolyte solution (2 mol/L). The newly produced hollow Co$_3$O$_4$ microspheres loaded on nickel foams, a platinum electrode, and a saturated calomel electrode (SCE) were used as the working electrode, counter electrode and reference electrode, respectively. The working electrode was composed of active Co$_3$O$_4$ materials (75 wt%), carbon black (15 wt%) and binder (PTFE, 10 wt%). The mixture was first coated onto the surface of a piece of nickel foam sheet (1 cm $\times$ 1 cm), and dried at 65$^\circ$C overnight. The sheets with active materials were finally pressed under 14 Mpa to obtain the working electrode. The loading weight of hollow Co$_3$O$_4$ microspheres on nickel foam sheet was 0.67 mg/cm$^2$. The cyclic voltammogram (CV), galvanostatic charge/discharge cycle tests and electrochemical impedance spectroscopy (EIS) were performed on a CHI 660E electrochemical workstation. The EIS measurements were performed from the frequency window of 0.01 to 100 KHz at an open-circuit potential with an ac perturbation of 5 mV.

3. Results and discussion

The morphologies of the as-obtained samples were characterized by field emission scanning electron microscope (FE-SEM) and transmission electron microscope (TEM). The SEM image shows the samples possess homogeneous diameters of ca. 500 nm and most of the samples are of intact spherical morphology (see in Fig. 1a). From the amplified SEM image of broken hollow microspheres in Fig. 1b, we could
evaluate that the shell thickness was about 50 nm. It can be learned from Fig. 1c that
the hollow $\text{Co}_3\text{O}_4$ microspheres exhibit distinct hollow feature and with a thin-wall
shell. In addition, the high magnification TEM image (as shown in Fig. 1d) distinctly
reveals the thin shell trait with the shell thickness about 50 nm. The structures of
hollow $\text{Co}_3\text{O}_4$ microspheres were further examined by high-resolution transmission
electron microscopy (HR-TEM) and selected area electron diffraction (SAED). On
one hand, as displayed in Fig. 1e, the d-spacings of the hollow microspheres are
approximately 0.28 and 0.24 nm, correspond to the $(220)$ and $(311)$ planes of cubic
$\text{Co}_3\text{O}_4$. The clear lattice fringes indicate that the microspheres are composed of a lot
of nanocrystalline with high crystallinity. The distinctive diffraction rings in Fig. 1f
further confirm their polycrystalline feature, which from the center could determined
to be $(220)$, $(311)$, $(511)$ and $(440)$ crystal planes.

![Fig. 1](image_url)

**Fig. 1** (a) Low magnification SEM image of hollow $\text{Co}_3\text{O}_4$ microspheres, (b) High
magnification SEM image of broken hollow microspheres, (c) Low magnification TEM image of hollow Co$_3$O$_4$ microspheres, (d) High magnification TEM image of hollow Co$_3$O$_4$ microspheres, (e) HR-TEM image of hollow Co$_3$O$_4$ microspheres, (f) SAED pattern of hollow Co$_3$O$_4$ microspheres.

On the other hand, the Raman analysis was also employed to characterize the optical properties of the hollow Co$_3$O$_4$ microspheres. As depicted in Fig. 2a, five apparent Raman peaks were located at 185, 480, 512, 593, 653 cm$^{-1}$, respectively. All of these peaks correspond to three $F_{2g}$, one $E_g$, and one $A_{1g}$ Raman-active modes of the Co$_3$O$_4$ microcrystals as marked in Fig. 2a. The values are in close proximity to standard microcrystalline Co$_3$O$_4$ powders.$^{29}$ This result indicates that the as-prepared samples are Co$_3$O$_4$ crystallizes in the form of the normal spinel structure with Co$^{2+}$ and Co$^{3+}$ being located at the tetrahedral and octahedral sites, respectively. Furthermore, samples synthesized at different hydrothermal temperatures were characterized by PXRD analysis. As illustrated in Fig. 2b, all the diffraction peaks could be indexed as the standard PDF card (JCPDS card No.43-1003) and agree with the characteristics of cubic spinel Co$_3$O$_4$ (Fd3m, a 0 = 8.804Å). There were no diffraction peaks from any other impurities, which implied the high purity of the Co$_3$O$_4$ microspheres. And the samples obtained at 100 °C exhibited poor crystallization properties. However, accompanied by the rise of hydrothermal temperature, the crystal plane intensity of (111) which was closely related to Co (II) of spinel Co$_3$O$_4$ slightly dropped. On the contrary, the intensities of (311), (400), (511) and (440) crystal plane related to Co
(III) increased visibly. This phenomenon reflected the fact that higher hydrothermal temperature would accelerate oxidation rate of Co (II). That also explains well why the researchers used to manufacture Co₃O₄ materials with two steps which were composed of synthesis of Co(OH)₂ precursor and high temperature calcination oxidation process (> 260 °C).

Fig. 2 (a) Raman spectra of hollow Co₃O₄ microspheres, (b) XRD patterns of products which were synthesized at different hydrothermal temperatures.

In this study, to obtain Co₃O₄ in one-step, we introduced cobalt complexes ammonia into the system. Here we shows the corresponding Nernst equations of Co (II) to Co (III) under two totally different reaction conditions:

\[
[\text{Co(H}_2\text{O)}]^{3+} + e^{-} \leftrightarrow [\text{Co(H}_2\text{O)}]^{2+}, \varphi^o = 1.80 \text{ V} \quad (1)
\]

\[
[\text{Co(NH}_3)]^{3+} + e^{-} \leftrightarrow [\text{Co(NH}_3)]^{2+}, \varphi^o = 0.18 \text{ V} \quad (2)
\]

Equation (1) represents the general conversion of Co (II) to Co (III) in ordinary alkaline solution. However, while the concentration of NH₃ is comparatively high in the solution, the former ligand (H₂O) of Co²⁺ would inevitably be replaced by NH₃ due to the much bigger coordination stable constant of latter one.³⁰ Obviously, we
successfully lowered the reaction thermodynamics of this transformation process by introducing NH$_3$. Therefore, Co$_3$O$_4$ materials could be synthesized in one-step with an extremely low hydrothermal temperature (120 $^\circ$C).

**Fig. 3** Formation schematic model of hollow Co$_3$O$_4$ microspheres.

Fig. 3 illustrates the synthesis schematic diagram of corresponding hollow Co$_3$O$_4$ microspheres. At the step (1), the [Co(NH$_3$)$_6$]$^{2+}$ (Fig. 3b) would generate at the room temperature. They were rapidly oxidized to [Co(NH$_3$)$_6$]$^{3+}$ (Fig. 3c) by O$_2$ resulted from immediate decomposition of H$_2$O$_2$ as illustrated in step (2). Then under the hydrothermal condition, on account of the low coordination stable constant of [Co(NH$_3$)$_6$]$^{2+}$ ($1.3 \times 10^5$),$^{31}$ there were simultaneous reactions took place at the same time at step (3). Under this circumstance, massive nanoparticles of Co$_3$O$_4$ were produced via the recrystallization process (as displayed in Fig. 3d). In the next place, the O$_2$ bubbles that were constantly produced due to the decomposition of H$_2$O$_2$ serve as center of core-shell structure formation. The vast bubbles consist in the reaction
solution tremendously favor the formation of hollow structure, which kept accordance with Zhang’s work. As shown in the step (4), temporary core-shell structures (Fig.3e) were formed, and numerous replication products emerged continuously. TEM images of intermediate products during the preparation process were also shown in Fig. 3e. It can be seen that the body of hollow Co$_3$O$_4$ microspheres were composed of small Co$_3$O$_4$ nanoparticles with size of several nanometers. Take into consideration of the abundant nitrate co-exsiting in the hydrothermal solution, they would affect the growth stage by selectively changing the growth kinetics of the different crystals. In addition, because of the large c-axis distance and charge balance, the nitrate is apt to insert into the Co-O bond, hence wrapped up Co$_3$O$_4$ nanoparticles. As a result, the disorder attraction of interatomic forces were deliberately interfered, newly-generated hollow intermediate structure were able to keep evolving in situ which isolated to each other. Under the twin impact of driving force of reducing surface energy and nitrate, encapsulated Co$_3$O$_4$ nanoparticles continued to grow and emerge with adjacent nanoparticles to forming hollow microspheres (Fig. 3f) as shown in step (5). Based on the standpoints of formation process mentioned above, H$_2$O$_2$ dosage and nitrate concentration seem to play irreplaceable mutual roles on facilitating the synthesis of hollow Co$_3$O$_4$ microspheres. Hence, we carried out two control experiments to investigate the effect of H$_2$O$_2$ and nitrate exerted on the Co$_3$O$_4$ crystal growth. However, the bubbles stemmed from the decomposition of H$_2$O$_2$ would serve as template of inner cavities of microspheres during hydrothermal condition. Taking into account the situation that a number of O$_2$ has already been consumed in the
oxidation conversion of $[\text{Co(NH}_3\text{)}_6]^{2+}$ to $[\text{Co(NH}_3\text{)}_6]^{3+}$, the $\text{H}_2\text{O}_2$ dosage is directly related to the size and quality of microsphere cavity. In a typical synthesis of hollow Co$_3$O$_4$ microspheres, the $\text{H}_2\text{O}_2$ dosage is 4 mL. However, the inadequate $\text{H}_2\text{O}_2$ dosage would lead to the fabrication of solid microspheres rather than hollow ones. Fig. 4a,b represents the TEM image of microsphere with the $\text{H}_2\text{O}_2$ dosage of 2 mL. The formation of solid Co$_3$O$_4$ microspheres (as shown in Fig.4b) is an evident that insufficient bubbles were unqualified for acting as the cavity template. While the $\text{H}_2\text{O}_2$ dosage was increased to 3 mL, hollow Co$_3$O$_4$ microspheres started to emerge and coexist with solid Co$_3$O$_4$ microspheres in final product as shown in Fig. 4c. Combined with the TEM image of Fig. 4d, it is observed that inner cavities were unevenly distributed due to bubbles deficiency. On the other hand, excess $\text{H}_2\text{O}_2$ would also brought negative effect into the synthesis process. As seen in Fig. 4e and 4f that although bubbles could act as the template of hollow structure, there was also a side-effect which can not be ignored. Disturbance of bubbles aggravated due to the increase of $\text{H}_2\text{O}_2$ (5 mL), which caused severe damages to the formation and growth of shell structures (as shown in Fig.4e). In this case, a large number of shell fragments coexisted with the integrated hollow microspheres in the final products. As the augment tendency of $\text{H}_2\text{O}_2$ dosage (6 mL) continued, a tremendous amount of bubbles would totally destroy the hollow structures, and as a result, blocky-shaped particles with voids generated instead of hollow Co$_3$O$_4$ microspheres (as displayed in Fig. 4g).
**Fig. 4** (a) Low magnification TEM image of microspheres with H$_2$O$_2$ dosage of 2 mL; (b) High magnification TEM image of individual solid microsphere with H$_2$O$_2$ dosage of 2 mL; (c) Low magnification TEM image of microspheres with H$_2$O$_2$ dosage of 3 mL; (d) High magnification TEM image of hollow Co$_3$O$_4$ microsphere with small cavity with H$_2$O$_2$ dosage of 3 mL; (e) Low magnification TEM image of microspheres with H$_2$O$_2$ dosage of 5 mL; (f) High magnification TEM image of cracked hollow Co$_3$O$_4$ microsphere with H$_2$O$_2$ dosage of 5 mL; (g) TEM image of product with H$_2$O$_2$ dosage of 6 mL.

Fig. 5 shows the TEM images of various samples, which were prepared with different nitrate concentrations but keep other parameters constant. It can easily be seen from Fig. 5a that the severe deficiency of nitrate (0.5 M) are unable to cover all the newly-produced Co$_3$O$_4$ nanocrystals in this situation. As a result, in spite of inner cavity caused by bubbles, the majority of nanocrystals reunited with each other to grow into blocky-shaped particles with voids (as shown in Fig.5b). Accompanied by
the increase of nitrate concentration (0.75 M), agglomerate phenomena were alleviated to some extent. As seen in Fig. 5c, incremental nitrate promoted the trend of hollow microspheres formation. With the assistance of nitrate inserting into Co-O bond, a substantial part of particles were of spherical morphology. Fig. 5d shows the TEM image of twin hollow microspheres that sharing the same internal cavity. The nitrate concentration of 1 M adopted in the typical synthesis process as shown in experimental section turned out to be optimum parameter that most benefits the preparation of hollow Co$_3$O$_4$ microspheres. As the concentration continued to increase, the amount of nitrate surpassed the appropriate dosage needed for covering Co$_3$O$_4$ microspheres with uniform size of 500 nm. As shown in Fig. 5e, some of the hollow Co$_3$O$_4$ microspheres possess bigger size than 500 nm and a magnified hollow Co$_3$O$_4$ microsphere shows the diameter of ca. 550 nm (as shown in Fig.5f). While the concentration of nitrate was increased to 1.5 M, the size of these as-obtained hollow Co$_3$O$_4$ microspheres were no longer homogeneous as shown in Fig. 5g and 5h, which could surely ascribed to the superfluous nitrate. Because under the hydrothermal condition, excess nitrate provided bigger cladding surface area for Co$_3$O$_4$ microspheres thus weakened the size restriction in the process of Co$_3$O$_4$ nanocrystals growth.
The electrochemical performances of the as-obtained hollow Co$_3$O$_4$ microspheres were investigated by CV, galvanostatic charge/discharge tests and EIS. The CVs of the hollow Co$_3$O$_4$ microspheres were recorded at different scan rates and in a potential range of -0.25 ~ 0.55 V (vs. SCE). All the curves show obvious pseudocapacitance features with a similar line type as shown in Fig. 6a. It can be observed in the graph that cathodic scan of CV curves did not match well with the corresponding anodic ones, which declares the polarizations exist in Faradaic redox reactions.$^{34}$

The pseudo-capacitances of the hollow Co$_3$O$_4$ microspheres were elucidated by galvanostatic charge/discharge tests in the potential range of 0 ~ 0.47 V. The specific capacitance of the supercapacitors could be evaluated from the charge/discharge tests together with the following equation.$^{35}$

**Fig. 5** (a), (c), (e), (g) TEM image and (b), (d), (f), (h) high magnification image of the as-prepared samples with nitrate concentration at 0.5, 0.75, 1.25, 1.5 M, respectively.
\[ C_m = \frac{I \Delta t}{m \Delta V} \]  \hspace{1cm} (3)

where \( C_m \) is the specific capacitance of the capacitor (F/g), \( I \) is the current of charge/discharge, and \( \Delta t \) is the discharge time period for the potential change \( \Delta V \), in volts, \( m \) is the mass load of the active material in electrode. Fig. 6b and Fig.6c shows the charge/discharge curves and specific capacitance values of pseudocapacitors made with as-prepared hollow \( \text{Co}_3\text{O}_4 \) microspheres measured at different current densities.

The specific capacitance of hollow \( \text{Co}_3\text{O}_4 \) microspheres was calculated to be 1227, 1169, 1116, 1035 F/g for various current density set at 1, 2, 4, 8 A/g, respectively. The dramatic performance advantage of hollow \( \text{Co}_3\text{O}_4 \) microspheres was attributed to the unique hollow nanostructure with thin shell which greatly increased the specific surface area of electrode materials. In this way, the active sites were more accessible to electrolytes and charge diffusion distances were largely shortened. However, in Wang’s latest work, they declared the synthesis of 3D-nanonet hollow structured \( \text{Co}_3\text{O}_4 \) nanomaterials at comparatively low temperature, even in a high concentration KOH solution (6 M), the sample exhibited a highest specific capacitance of 820 F/g at different scan rates. In a period of time ago, Meher also obtained ultralayered \( \text{Co}_3\text{O}_4 \) nanostructures with the specific capacitance of 548 F/g. The great improvement of maximum specific capacitance of hollow \( \text{Co}_3\text{O}_4 \) microspheres over 3D-nanonet hollow structured \( \text{Co}_3\text{O}_4 \) nanomaterials and ultralayered \( \text{Co}_3\text{O}_4 \) nanostructures could be ascribed to two main aspects. Firstly, the thin shell with nanoscale thickness not only benefited the ion transport but also provided far more electrochemical active sites than traditional nanostructures. Therefore, the efficiency of electrochemical reactions...
increases dramatically. Secondly, the shell were relatively fragile due to their ultrathin thickness, they would inevitably be broken in preparation and subsequent post-treatment process, which could be supported by TEM images in both Figure 1a, 1b. In this way, the potential accessible active sites of hollow Co$_3$O$_4$ microspheres became even more.

Fig. 6 (a) The CV curves of the hollow Co$_3$O$_4$ microspheres recorded at different scan rates. (b) The first time charge/discharge curves of the hollow Co$_3$O$_4$ microspheres measured at different current densities. (c) Specific capacitance values of hollow Co$_3$O$_4$ microspheres at different current densities. (d) Specific capacitance versus cycle number of hollow Co$_3$O$_4$ microspheres at a galvanostatic charge and discharge current density of 2 A/g. The inset is EIS spectras of hollow Co$_3$O$_4$ microspheres before and after 1000 cycles.

Cycling stability is another key index for the supercapacitors possess application
potentials. As seen in Fig. 5d, after cycling for 1000 times, the capacitance of electrode made of hollow Co$_3$O$_4$ microspheres only slightly decreased to approximately 97.5% of its maximum value, which indicated its excellent reversibility. This result also consisted with the EIS curve in Fig.6d inset. Obviously the internal resistance of the solution almost remained the same after the cycling test, and the charge transfer resistance undergone a slight increase. The internal cavity of hollow Co$_3$O$_4$ microspheres could provide buffer for the thermal expansion during electrochemical process. And thin shell of hollow Co$_3$O$_4$ microspheres also are in favor of keeping solution evenly by facilitating ion transport. Therefore, even after a long cycle of 1000 times, the electrode structure basically kept intact.

4. Conclusions

In this report, hollow Co$_3$O$_4$ microspheres with thin shell of 50 nm were synthesized with one-step hydrothermal method in low temperature (120 °C). By means of taking advantages of mutual influences of nitrate and H$_2$O$_2$, hollow Co$_3$O$_4$ microspheres with thin shell were obtained for the first time with the absence of morphology template, organic reagent and additional calcination. Subsequent electrochemical evaluation showed that hollow Co$_3$O$_4$ microspheres possess a maximum specific capacitance of 1227 F/g and 97.5 % of the initial value even after a long cycling test of 1000 times. This tremendous superiority could be ascribed to its hollow nanostructure and thin shell, which not only greatly increased the active sites of electrode materials and shortened ion transfer distance but also offered buffer for the thermal expansion
during electrochemical process. This study projected a light beam on the novel thought of synthesis control of nanostructure relying on managing micro-reaction conditions.

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