1 Introduction

With the energy crisis and the increasing concerns about the environment, better energy storage materials are urgently needed. Supercapacitors are considered as one of the most promising candidates for energy storage and have attracted significant attention due to their high power capabilities, low cost and long cycle life.\(^1\) Nanostructured transition metal oxides (such as Co\(_3\)O\(_4\), NiO, MnO\(_2\), and RuO\(_2\)) are novel materials for supercapacitors because of their exceptional electrochemical (pseudo-capacitive) properties. Co\(_3\)O\(_4\) is particularly attractive in this area because of its high theoretical capacity. When falling in the nanosized regime, it is expected to lead to even more attractive properties. As an excellent catalyst and battery cathode material, Co\(_3\)O\(_4\) nanomaterials have been widely used in photocatalytic biosensing and supercapacitors.

Over the past decade, nanostructured Co\(_3\)O\(_4\) materials are usually synthesized through a two-step process.\(^7\text{-}10\) Initially, the precursors with different structures are mainly synthesized by hydrothermal approaches, and then Co\(_3\)O\(_4\) were obtained by thermal decomposition at elevated temperatures. However, it is difficult to control the size (especially nanosize), morphology and size distribution of these products obtained by these conventional methods.

Herein, we describe a novel one step shape-controlled synthesis of uniform Co\(_3\)O\(_4\) nanocubes with a size of 50 nm with the existence of mesoporous carbon nanorods (meso-CNRs). In this synthesis process, meso-CNRs not only act as a heat receiver to directly obtain Co\(_3\)O\(_4\) eliminating the high-temperature post-calcination, but also control the morphology of the resulting Co\(_3\)O\(_4\) to form nanocubes with uniform distribution. More strikingly, mesoporous Co\(_3\)O\(_4\) nanocubes are obtained by further thermal treatment. The structure and morphology of the samples were characterized by scanning electron microscopy, transmission electron microscopy and X-ray diffraction. A possible formation mechanism of mesoporous Co\(_3\)O\(_4\) nanocubes is proposed here. Electrochemical tests have revealed that the prepared mesoporous Co\(_3\)O\(_4\) nanocubes demonstrate a remarkable performance in supercapacitor applications due to the porous structure, which endows fast ion and electron transfer.
dissolved in water with vigorous stirring. Meso-CNRS were added into this solution under ultrasonication. Then, the mixture was transferred to a Teflon-lined stainless steel autoclave and the hydrothermal process was performed at 120 °C for 12 h. The product was collected by filtration and washed several times with pure water and then dried at 60 °C for 12 h under vacuum. Through those procedures, the Co$_3$O$_4$ particles were obtained. In the second step, the as prepared Co$_3$O$_4$ particles were heated at 300 °C for 2 h in air with a rate of 10 °C min$^{-1}$ in a muffle stove to remove meso-CNRS and to obtain the mesoporous Co$_3$O$_4$.

2.3 Characterization

Scanning electron microscopy (SEM) observations were carried out on a Hitachi S-4800 field emission scanning electron microscope operated at 3.0 kV. Transmission electron microscopy (TEM) observations were carried out on a JEOL JEM-2010 transmission electron microscope at an acceleration voltage of 200 kV. N$_2$ adsorption–desorption measurements were carried out on a V-Sorb 2800P surface area analyzer at 77 K using the volumetric method and samples were degassed at 150 °C under vacuum overnight before measurements. The Brunauer–Emmett–Teller (BET) specific surface areas were calculated by using adsorption data in $P/P_0 = 0.04–0.20$ (six points collected). Pore size distributions were estimated from adsorption branches of the isotherms by using the Barrett–Joyner–Halenda (BJH) method. Powder X-ray diffraction (XRD) measurements were carried out on a Bruker Smart APEX CCD diffractometer at 40 kV and 20 mA using Cu-K$_\alpha$ radiation ($\lambda = 1.54$ Å) from 10° to 80° at a scanning rate of 5° min$^{-1}$.

2.4 Electrochemical measurement

A typical three-electrode experimental cell was used for measuring the electrochemical properties of the working electrode. For comparison, a pure Co$_3$O$_4$ nanocube sample was prepared by the same procedure in the absence of meso-CNRS. The Co$_3$O$_4$ nanocubes or mesoporous Co$_3$O$_4$ nanocubes served as the working electrode, while a platinum foil electrode and a standard calomel electrode (SCE) were used as the counter and reference electrodes, respectively. All electrochemical measurements were carried out in 6.0 M KOH solution as an electrolyte. Cyclic voltammetry (CV), galvanostatic charge–discharge, and electrochemical impedance spectroscopy (EIS) were carried out on the CHI660 electrochemical work station (Chenhua, Shanghai).

3 Results and discussion

3.1 Characterization of the morphology of meso-CNRS and Co$_3$O$_4$ nanocubes

Fig. 1a and b present the SEM images of the as-prepared nanorods of the nickel dimethylglyoximate complex before and after carbonization, respectively. The SEM image shows that the surface of the as-prepared nanorods of nickel dimethylglyoximate is much smooth. After carbonization, the surface of the NiO(Ni)/C composites is decorated with a large number of convex particles. After the NiO or Ni nanoparticles were removed by HCl solution, a large number of mesopores can be clearly observed and randomly distributed on the framework of the meso-CNRS (Fig. 1c), which were originally occupied by NiO or Ni species. This observation indicates that meso-CNRS were successfully fabricated by this crystalline and etching strategy. Fig. 1d shows the SEM image of the as-prepared nanocubes/meso-CNRS by the hydrothermal synthesis process. Many cube-like nanoparticles with uniform size-distribution are observed on the surface of meso-CNRS.

3.2 Morphology-controlled growth

By fixing the concentration of meso-CNRS (0.025 mg mL$^{-1}$), the effect of the concentration of CoCl$_2$·6H$_2$O was studied, and SEM examination was conducted. When the concentration of CoCl$_2$·6H$_2$O is 0.00125 mmol mL$^{-1}$, the SEM image indicates that the resulting sample consists of uniform nanocubes with the size of about 50 nm (Fig. 2a). With the increase of CoCl$_2$·6H$_2$O concentration to 0.005 mmol mL$^{-1}$, the obtained sample presents needle-like nanorods with diameters about 200 nm and length up to 5 μm, and many nanoparticles with a size of about 50 nm can be observed (Fig. 2b). Further increasing the concentration of CoCl$_2$·6H$_2$O to 0.01 mmol mL$^{-1}$, all of the resulting products are needle-like nanorods with sharp end and smooth surface, as shown in Fig. 2c. When the concentration of CoCl$_2$·6H$_2$O increased to 0.025 mmol mL$^{-1}$, the 3D-sisal-like architecture with an average diameter of 15 μm appeared (Fig. 2d). It can be found that this sisal-like architecture is formed by many needle-like nanorods growing radially from the core; and these nanorods were about 100–300 nm wide and 5–10 μm long with sharp end. It indicates that the CoCl$_2$·6H$_2$O
concentration has a large effect on the morphology of the resulting samples. When the concentration of CoCl$_2$·6H$_2$O exceeds the support capability of meso-CNRs, the free Co$^{2+}$ would coordinate with the molecular or other anions in solution and homogeneous nucleation and growth occurred because of strong coordination ability of Co$^{2+}$. As a result, needle-like nanorods and 3D-sisal-like architecture appeared with increase of the concentration of CoCl$_2$·6H$_2$O.

Fig. 3 shows the XRD patterns of the obtained nanocubes and 3D-sisal-like architecture before and after calcination. Fig. 3a indicates that the as-prepared nanocubes have identical peaks, which can be perfectly indexed to cubic Co$_3$O$_4$ (JCPDS card no. 42-1467). As expected, after calcination at 300 °C, the peaks in Fig. 3a (top line) become sharper and clear than the down line, which indicates the improved crystallinity. In contrast, the XRD pattern of the as-prepared 3D-sisal-like architecture obtained at a high concentration of CoCl$_2$·6H$_2$O (0.025 mmol mL$^{-1}$) demonstrates that the sample is a mixture of Co$_3$O$_4$ (JCPDS card, no. 42-1467), Co(CO$_3$)$_{0.35}$Cl$_{0.2}$[OH]$_{1.1}$·1.74H$_2$O (JCPDS card, no. 38-0547), Co(OH)$_2$ (JCPDS card, no. 02-0925) and Co(NH$_3$)$_6$Cl$_2$·H$_2$O (JCPDS card, no. 22-0587) (Fig. 3b, top line). After calcination at 300 °C, the sample has identical peaks (Fig. 3b, down line), which correspond well to the cubic Co$_3$O$_4$ (JCPDS card no. 42-1467). It may be come from the fact that the meso-CNRs can serve as the second heater to absorb enough energy, which can combine and boost the temperature of the precursor in situ. When the concentration of meso-CNRs is high enough compared to CoCl$_2$·6H$_2$O, it can result in the formation of Co$_3$O$_4$ directly by the one step hydrothermal process. These phenomena coincide well with the literature.$^{12,13}$

To get more insight into the effect of meso-CNRs on controlling the morphology and size distribution of the synthesized samples, we observed the samples obtained at different concentrations of meso-CNRs at the fixed concentration of CoCl$_2$·6H$_2$O (0.00125 mmol mL$^{-1}$), SEM examination was conducted (Fig. 4). Fig. 4a is the image of the sample obtained without meso-CNRs. Without the existence of meso-CNRs, the resulting nanoparticles are irregular with different sizes. When a little amount of meso-CNRs (0.0175 mg mL$^{-1}$) was added into the solution, nanocubes were observed and the nanoparticles became very uniform in size of about 50 nm (Fig. 4b). With the increase in concentration of meso-CNRs, such as 0.025 mg mL$^{-1}$ or 0.05 mg mL$^{-1}$, the nanocubes still remained (Fig. 4c) but aggregation occurred (Fig. 4d). It can be concluded that the surface area and porosity of the meso-CNRs play an important role in the formation of uniform nanocubes. First, when meso-CNRs were added into the solution containing Co$^{2+}$, the randomly distributed functional groups in meso-CNRs could serve as anchor sites for nucleation of nanocubes (as shown in Fig. 1d). Second, as the second heater, meso-CNRs can absorb heat and boost the temperature so as to enable the samples to couple directly with thermal fields. Hence, when the amount of meso-CNRs was added too much, the meso-CNRs absorb too much heat to accelerate the growth speed of nanocubes and result in some aggregation.

Fig. 5a and b show the magnified SEM and TEM images of the as-prepared Co$_3$O$_4$ nanocubes. It can be seen that the nanocubes are very regular with uniform size distribution (~50 nm). Excellent crystallinity of the nanocubes is also
after calcination is 15.1 m$^2\text{g}^{-1}$ and 25.8 m$^2\text{g}^{-1}$, respectively, and increased more than 50%. Fig. 5d shows the pore size distribution of Co$_3$O$_4$ nanocubes before and after calcination. Before calcination, the pore size is primarily in the range of 50–60 nm which may be due to interspaces produced by accumulation of Co$_3$O$_4$ nanocubes, and only little distribution in the range of 4–5 nm. After calcination, the pore size is primarily in the range of 2–3 nm with a narrow distribution. These N$_2$ sorption results are corresponding well with the previous microscopy findings (Fig. 5b and c).

Meso-CNRs can absorb enough energy to convert the precursor in nanosize to Co$_3$O$_4$ by hydrothermal treatment, however, many water molecules are enclosed in the crystal lattices and the nanocube is loose. Similar to the literature,$^{14,15}$ water molecules released from the nanocubes and Kirkendall effect result in the solid-state crystal re-construction process occurred during calcination. As a result, mesoporous nanocubes are formed. According to the above analysis, such mesopores are created by the release of lattice water molecules and volume contraction during crystal re-construction.$^{16,17}$

### 3.3 Electrochemical analysis

The electrochemical performances of mesoporous Co$_3$O$_4$ nanocubes are evaluated as the working electrode for supercapacitor applications. The Co$_3$O$_4$ nanocubes were fixed on rectangular nickel foam, and the loaded weight of the Co$_3$O$_4$ nanocubes is about 0.5 mg cm$^{-2}$. Fig. 6a presents the cyclic voltammetry (CV) curves of the Co$_3$O$_4$ nanocube electrode at scan rates of 5, 10, 20, 50 and 100 mV s$^{-1}$, respectively. The CV curves are different from the ideal rectangular shape of the typical electric double-layer capacitance. There are a couple of redox peaks of Co$_3$O$_4$, which suggest that the capacitance is confirmed with high-resolution TEM images (Fig. 5b, inset). More interestingly, when the cubic sample was calcined at 300 °C, mesopores in the nanocubes were observed, as shown in Fig. 5c.

Nitrogen sorption was used for characterization of the inner structure of the obtained Co$_3$O$_4$ nanocubes before and after calcination. The specific surface area of samples before and after calcination is 15.1 m$^2\text{g}^{-1}$ and 25.8 m$^2\text{g}^{-1}$, respectively, and increased more than 50%. Fig. 5d shows the pore size distribution of Co$_3$O$_4$ nanocubes before and after calcination. Before calcination, the pore size is primarily in the range of 50–60 nm which may be due to interspaces produced by accumulation of Co$_3$O$_4$ nanocubes, and only little distribution in the range of 4–5 nm. After calcination, the pore size is primarily in the range of 2–3 nm with a narrow distribution. These N$_2$ sorption results are corresponding well with the previous microscopy findings (Fig. 5b and c).

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mainly from the pseudocapacitance of Co$_3$O$_4$. In addition, increasing the scan rate leads to further augment of the CV curve and the redox peaks, indicating that the redox reactions of Co$_3$O$_4$ are rapid.

Fig. 6b depicts the charge–discharge behavior of the Co$_3$O$_4$ nanocube electrode between $-0.35$ V and 0.5 V at different current densities. The specific capacitance can be calculated as follows: $C_m = \frac{\Delta I}{\Delta V_m}$. According to the above equation, the specific capacitance of the Co$_3$O$_4$ nanocube electrode is calculated to be about 350, 281, 220, 210 and 160 F g$^{-1}$ at the current densities of 0.2, 0.3, 0.6, 1.0 and 2.0 A g$^{-1}$, respectively (Fig. 6c), which is much higher than the pure Co$_3$O$_4$ nanocubes (120 F g$^{-1}$ at 0.2 A g$^{-1}$, Fig. S1†). The cycling behavior indicates that after a long period of charge–discharge at a current density of 2.0 A g$^{-1}$, the charge–discharge curves still remain undistorted and essentially symmetric (inset of Fig. 6c). Electrochemical impedance spectroscopy (EIS) was also employed to characterize the pure meso-CNRs, pure Co$_3$O$_4$ nanocubes and mesoporous Co$_3$O$_4$ nanocube electrodes. As shown in the Nyquist plots (Fig. 6d), the equivalent series resistance (ESR) of the mesoporous Co$_3$O$_4$ nanocube electrode is much smaller than that of the pure Co$_3$O$_4$ nanocubes, pure meso-CNR electrode, indicating a lower diffusion resistance and charge-transfer resistance.

4 Conclusion

In this study, we demonstrate a simple and novel one step shape-controlled synthesis of Co$_3$O$_4$ nanocubes with uniform diameter and high crystallinity with the help of meso-CNRs. Herein, meso-CNRs serve as a heat receiver and anchor sites for nucleary of nanocubes. In addition, mesoporous Co$_3$O$_4$ nanocubes were formed after calcination without the need for any template or surfactant. A possible formation mechanism of mesoporous Co$_3$O$_4$ nanocubes is proposed. The Kirkendall effect results in the solid-state crystal re-construction process, which is responsible for the formation of mesoporous Co$_3$O$_4$ nanocubes. The unique porous structure endows fast ion and electron transfer, leading to a superior pseudo-capacitive performance, and the electrochemical utilization of Co$_3$O$_4$ was improved.

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